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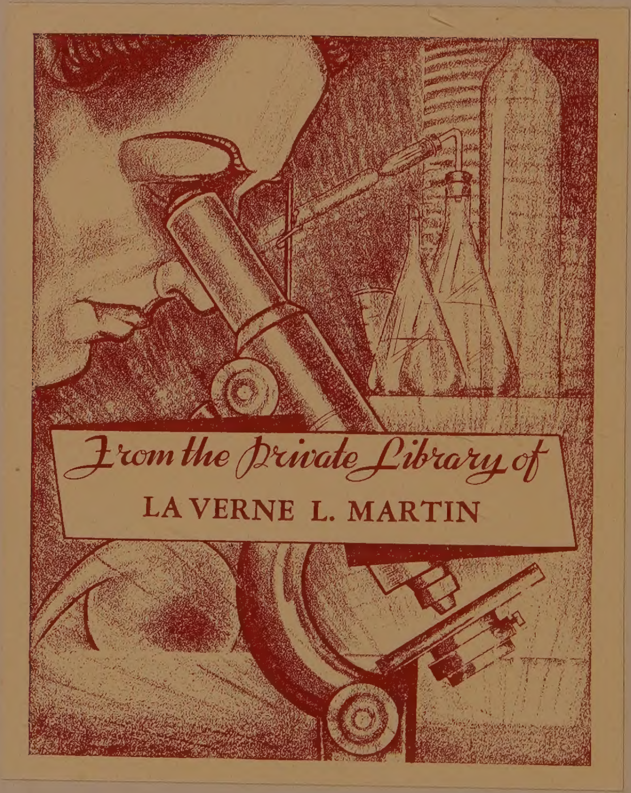
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THE CHEMICAL ANALYSIS
OF ROCKS

Author's Workbench in the Geophysical Laboratory *Frontispiece*

THE CHEMICAL ANALYSIS OF ROCKS

BY

HENRY S. WASHINGTON, Ph.D.

FOURTH EDITION
REWRITTEN AND ENLARGED

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HENRY S. WASHINGTON

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PREFACE TO THE FOURTH EDITION

The present edition has been thoroughly revised and much of it has been rewritten. It is also somewhat enlarged, mostly by the incorporation of descriptions of new methods and of the use of new reagents. The number of these is constantly increasing, and it would seem that the rock-analyst of the future will carry out many, if not most, gravimetric separations and determinations by the use of specific reagents (mostly organic, such as cupferron and dimethylglyoxime), together with special volumetric or colorimetric methods for certain constituents, as we now do for iron and titanium. I have tested all the new methods and reagents described, except in some cases noted in the text.

The various methods and procedures have been treated with even greater detail than in previous editions, in accordance with the main purpose of the book, that of being a practical guide for the beginner or student, so that he may be able to work alone. As before, it is to be understood that silicate igneous rocks are meant when ''rocks'' are spoken of. References to recent literature are frequent, but they are not to be regarded as in any way complete, although it is hoped that the most useful papers have been cited. Preference has been given to publications in the United States. The theoretical side has been but lightly touched on, as the book is essentially one for practice rather than one of theory.

All temperatures are in centigrade degrees. The factors used in the calculations and in the table on page 277 are those in accordance with the International Table of Atomic Weights for 1928.[1]

''Cubic centimeter'' (c.c.) is used instead of ''milliliter'' (ml.). This follows the practice of the leading chemical journals in this country and England.[2] I am also old-fashioned enough to prefer the spellings sulphur and sulphate to sulfur and sulfate. Similarly burette and pipette are used instead of buret and pipet. The names baria, magnesia, titania, zirconia, etc. are used instead of barium oxide, titanium dioxide, etc. They are much shorter than the former and are readily understandable. A protest against the use of chloroplatinate, fluosilicate, etc. is registered on page 231, although in this case I now conform to the present general chemical usage.

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[1] Jour. Am. Chem. Soc., **50**, p. 615, 1928.

[2] Cf. Treadwell-Hall, p. 441; Hillebrand-Lundell, p. 121. The abbreviation "c.c." is more logical than "cc." because cubic centimeter consists of two words: it is used by the English Journal of the Chemical Society.

It is again a pleasure to express my grateful obligations to Dr. Arthur L. Day, Director of the Geophysical Laboratory, for his permission to undertake the preparation of this edition while a member of its staff. I also acknowledge gratefully my indebtedness to Miss Mary G. Keyes, my former assistant at the Geophysical Laboratory, for the chemical analysis of rocks. The revision has been greatly furthered by her suggestions, and she has aided much in the preparation of the manuscript. To my colleagues at the Geophysical Laboratory I am deeply indebted for much friendly and valuable criticism and information. Of these I would mention Drs. L. H. Adams, E. T. Allen, C. N. Fenner, H. E. Merwin, G. W. Morey, Eugene Posnjak, E. S. Shepherd, and, especially, E. G. Zies, who has critically read much of the manuscript. I would also thank Drs. Charles E. Munroe, G. E. F. Lundell, G. Steiger, and W. M. Thornton, Jr., for useful suggestions. Mr. J. Harper Snapp, of the Geophysical Laboratory, very kindly made the photograph of my work-bench, which appears as the frontispiece. Finally, my obligations to the work and to the inspiration of the late Dr. W. F. Hillebrand will be evident in this edition as in previous ones.

HENRY S. WASHINGTON.

Geophysical Laboratory,
Carnegie Institution of Washington
June, 1930.

PREFACE TO THE FIRST EDITION

The object of this book is to present to chemists, petrologists, mining engineers, and others who have not made a particular study of quantitative analysis, a selection of methods for the chemical analysis of silicate rocks, and especially those of igneous origin. While the publication of such a work may seem superfluous in view of the existence of Hillebrand's treatise on this special topic, yet justification may be found in the fact that the latter is intended, not so much for one who is not very conversant with the subject, as for the practiced analyst, to whom it is an indispensable guide.

A further reason for its appearance is that, apart from Hillebrand's book and a paper by Dittrich, there does not seem to exist any separate modern treatise on the chemical analysis of rocks. The space devoted to this branch of analysis in the textbooks is usually very small, and the various methods are widely scattered and often inadequately described. This is especially true in regard to the minutiæ of manipulation and precautions to be observed, and to the determination of elements which, though usually accounted rare, have of late years been shown to be very common rock constituents. This neglect is rather striking in view of the prominence given in the last decade or so to the chemical composition of igneous rocks.

There is an increasing number of geologists, petrologists, chemists, and others, who are desirous of making chemical analyses of rocks, but who have had little or no experience in the subject, except that gained in the ordinary course of quantitative analysis, in which the study of silicates is usually confined to the examination of a feldspar or some such simple mineral. It is for the benefit of this class of students that the present book is written. The general plan adopted therefore is, not to attempt a complete treatise on rock analysis, but to present only certain methods which have proved simple and reliable in the experience of the chemists of the U. S. Geological Survey and of my own. The more important of these, and some of the principal operations, are described with great explicitness. Many small details of manipulation are gone into which are omitted by

Hillebrand and the textbooks as unnecessary, a knowledge of them being either presupposed or their demonstration left to the instructor.

In this way it is hoped that it will be possible for an intelligent student, with some knowledge of chemistry and a little analytical training, to be able to complete a satisfactory analysis of an ordinary silicate rock, without personal instruction and after comparatively short practice. To the expert analyst, therefore, the book will contain much that is superfluous, but for this no apology is offered. What are superfluities to him will, it is hoped, be welcome to the novice.

It is assumed that silicate igneous rocks will be the most frequent objects of investigation. At the same time, the methods described serve equally well for most silicate metamorphic and sedimentary rocks. Such rocks as saline deposits, coals and others containing organic matter are not considered. The methods are not generally adapted to the analysis of ores, which, with such constituents as sulphides, arsenides, and other compounds of the heavy metals, often call for different and more complex means of separation than are here given. The same is true of many minerals, though the methods found in the following pages are those appropriate to the analysis of most silicates. The analysis of meteorites also demands the employment of special methods, and in most cases these bodies are of such character that their examination should not be undertaken by the inexperienced, especially if only a limited supply of material is available.

The methods selected are, in general, those adopted by the chemists of the U. S. Geological Survey, and which in their essentials I have employed in my own scientific work for a number of years. Some modifications have been made, chiefly in the direction of simplification and the elimination of certain refinements that do not seem called for when the object of the volume is considered. There is no attempt at the introduction of new methods[1] or the description of alternative ones which, either on theoretical grounds or on account of practical difficulties, are deemed to be less well adapted to the needs of students than those that are here given. Theoretical discussion will be limited to that which may seem necessary to make clear the principles of certain methods or the reasons for their selection.

I have also endeavored to point out to the student the importance of chemical analyses for the study of rocks, and their possible bearing on some of the broad problems which form the objects of the science of petrology. In other words, it has been sought to emphasize the fact that petrographic classifications and the study of textures and of minerals in thin sections are not the sole aims of the science, but that, supplemented by a knowledge of the chemical composition of igneous rocks, they are only means to broader ends. I can only express the hope that this little book will aid in the progress of petrology, by leading to an increase in the knowledge of chemical analysis among petrologists and rendering our data in the way of rock analyses of superior quality more numerous.

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[1] This does not apply to succeeding editions or the present one.

The great obligations under which I am to Dr. Hillebrand's work are evident throughout and are most gratefully acknowledged. The textbooks of Fresenius, Classen, Treadwell, and Jannasch have also been consulted, and the book is indebted to them in many ways. It is also a pleasure to express my obligations to several friends for valuable advice and assistance, and especially to Prof. S. L. Penfield and Prof. L. V. Pirsson, to whom my first knowledge of, and training in, quantitative analysis are due. A number of most useful hints in manipulation were learned from these two analysts, all of which could not be specifically mentioned in their proper places, but which are acknowledged here. Acknowledgments are also due to the Trustees of the Carnegie Institution for permission to publish an analysis made under their auspices.

The factors used in calculations are those given by Cohn in his recent translation of Fresenius' "Quantitative Analysis." All temperatures are given in centigrade degrees. The metric system is used generally, except in dealing with such pieces of apparatus as are usually sold in this country on the basis of English measurements.

HENRY S. WASHINGTON.

Locust, N. J.,
May, 1904.

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THE CHEMICAL ANALYSIS OF ROCKS

PART I

INTRODUCTION

1. Importance of Chemical Analyses

The science of geochemistry[1] is based in large part on the chemical composition of igneous rocks, and the methods of analysis described in this book apply especially to igneous rocks. These rocks have been formed by the solidification of molten magma,[2] so that the portion of it that consolidates as rock determines, within limits, the actual mineral composition of the rock. Hence, chemical analysis of the rock itself gives knowledge of the magma from which it has been derived, volatile components being left out of account, to a large extent.

Knowledge of the chemical composition of igneous rocks is also necessary, indeed fundamental, for the study of such petrologic problems as differentiation, consanguinity, petrographic provinces (comagmatic regions), rock weathering, and petrogenesis. We are thus led to consider igneous rocks[3] as products of evolution in the sense of Herbert Spencer's definition.

The chemical composition of the igneous rocks may also enter into problems of volcanology, seismology, isostasy, continental drift, and the origin of the solar system.

To the petrographer, who deals especially with the descriptive and systematic aspects of the science of rocks, the chemical analysis of igneous rocks is of great importance.[4] Chemical analyses of the rocks described form part of almost all petrographic papers; and they are now inserted as an essential part of the description, not, as formerly, only an ornamental and somewhat perfunctory adjunct.[1] They are indeed of fundamental importance for the classification of igneous rocks, as is evident in many recent publications.

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[1] Cf. F. W. Clarke, The Data of Geochemistry, U. S. Geol. Survey, Bull. 770, 1924.

[2] Cf. A. Holmes, The Nomenclature of Petrology, 1920, p. 148.

[3] Cf. R. A. Daly, Igneous Rocks and their Origin, New York, 1914; N. L. Bowen, The Evolution of the Igneous Rocks, Princeton, 1928.

[4] Cf. A. Holmes, Petrographic Methods and Calculations, London, 1921, p. 384; S. J. Shand, Eruptive Rocks, London and New York, 1927, p. 102.

For this reason, it must be emphasized that every petrologist and every petrographer should be able to make, or have had some practice in making, chemical analyses of igneous rocks.[2] Such practical acquaintance with analytical methods should form a necessary part of his curriculum, training, and technical equipment, as well as his ability to use the microscope for the study of thin sections. He will thus be able to judge wisely of the quality and reliability of a rock analysis,[3] and so not fall into error through blind acceptance of the analysis. At the present time, with wider knowledge and greater application of the importance of chemical analyses for petrology, the crude student analyses of the early days are beginning to be looked on with suspicion, and are much less used than of old.

For the proper understanding and study of the theoretical aspects and relations of igneous rocks, and of their genesis, a knowledge of some of the principles of physical chemistry is necessary. It is obvious that a knowledge of the chemical composition of igneous rocks is essential for such physicochemical studies. The properly equipped petrologist should therefore be acquainted with physical chemistry as well as with chemical analysis. On the other hand, the study of igneous rocks may be of service to the sister science, because the petrologist deals with solidified solutions or high temperature liquid systems, under conditions of mass, time, temperature, and pressure, often in the presence of dissolved gases, some of which conditions it is impossible to reproduce severally or conjointly in the laboratory.

Although our knowledge of metamorphic rocks is as yet not so far advanced as that of igneous rocks, chemical analysis plays, likewise, an important part in their study, interpretation, and classification.[4] To a certain extent the same is true of the sedimentary rocks. Our knowledge of meteorites, also, is largely dependent on knowledge of their chemical composition.[5]

---

[1] Cf. Washington, Prof. Paper **99**, p. 10.

[2] A. Holmes (*op. cit.*, p. 385) expresses himself to the same effect.

[3] Cf. Washington, Prof. Paper **99**, pp. 19–22.

[4] Carbonate rocks are not considered in this book; for their analysis one may consult Hillebrand, Bull. **700**, or Hillebrand–Lundell.

[5] The student will find an example of the procedures used in the analysis of

As regards the economic side of geology, such as the origin and formation of ores and useful mineral deposits, a knowledge of the chemical composition of the associated igneous or metamorphic rocks is important. This refers not only to their main features, but to the occurrence in them of the less abundant elements, which by processes of concentration may become commercially available as ores.

Inasmuch as almost all igneous rocks are silicate rocks, many of the methods and procedures described in this book are applicable to the analysis of silicate minerals. But rocks in general are more complex than most minerals. On the other hand, many silicate minerals demand special treatment because certain constituents that are of minor importance, quite negligible, or even non-existent in rocks, may be major constituents in minerals.[1]

2. General Character of Analyses[2]

The fulfilment of two conditions is essential to the value of a rock analysis: the specimen must be representative of the rock-mass, and the analysis itself must represent truly the composition of the specimen selected. The more closely both of these conditions are met the greater will be the value of the analysis.

The representative character of the specimen is determined by the character of the rock-mass, as influencing both its selection and the amount of material taken for analysis. These points will be discussed subsequently (p. 77).

Assuming that the sample is representative of the rock-mass, the degree of correspondence between the figures yielded by the analysis and the chemical composition of the rock is dependent on the two factors of accuracy and completeness.

Accuracy of Analyses.—By accuracy is meant the degree of precision with which the constituents sought for are determined, irrespective of whether or not all those present have been determined or separated one from another. The accuracy of an analysis is dependent upon the methods used and upon the ability of the analyst to execute the various processes successfully. The purity of the reagents and the adequacy of the apparatus are also factors.

---

meteorites by the chemists of the U. S. National Museum and by Dr. J. E. Whitfield in: G. P. Merrill, U. S. Nat. Mus., Bull. **149**, p. 57, 1930. See also G. T. Prior, Min. Mag., **17**, p. 22, 1913; **17**, p. 132, 1914; **18**, p. 349, 1919.

[1] Cf. Hillebrand–Lundell, p. v.

[2] This and the next two sections are a somewhat summarized statement of the discussion published in Prof. Paper **99**, U. S. Geol. Survey, 1917, pp. 10–18.

No analytical method is capable of yielding results that are absolutely accurate, any more than it is possible to construct a mathematically exact geometrical figure. Certain sources of error are inherent in all analytical determinations, some of a general nature, and others of a character dependent on the method employed. The analyst must rest content with reducing these to a minimum, by selecting methods that are known to be reliable. In this he cannot do better than follow the chemists of the U. S. Geological Survey, whose experience is of the widest, and who have set up a standard of analytical methods and practice for the analysis of rocks that is of the first order of excellence.

But the selection of proper methods is not the only desideratum. The procedure must be carried out in a proper way, one that does not lead to errors of a mechanical kind which may easily vitiate the results of the most accurate method. In the matter of procedure the analyst himself and the reagents are also most important factors. The analyst should have not only sufficient knowledge of the facts of chemistry and the principles of analysis to work understandingly but also the dexterity and manipulative skill to enable him to carry out the various processes successfully. Though it may be true of some analysts that, like poets, they are born, not made, yet granted intelligence, some general chemical knowledge, and a fair amount of dexterity and application, the necessary manipulative skill will come with practice, often in a surprisingly short time.

The analyst must beware of falling into careless habits or allowing the analysis to become merely routine work.[1] Carelessness is as fatal to good results as poor methods or impure reagents. During the whole process of an analysis attention should be paid to every point of theory and manipulation, the influence of the various conditions or constituents should be considered, and indeed the analysis should be carried out from beginning to end with intelligent interest. This will turn into pleasure what would otherwise be a dull and monotonous succession of precipitations, filtrations, ignitions, and weighings, which, as has been justly said, are not chemical analysis.

That *conscientiousness, a strict regard for the truth,* and a firm determination to accept no result in any way doubtful, *are essential,* goes without saying, and their importance cannot be too strongly insisted on. As Fresenius emphasizes,[1] in a paragraph that it is well for all students and many analysts to read and take to heart, if one is not *positively convinced* of the accuracy of a result, the operation, or even the whole analysis, should be repeated. If the analyst is not conscientious enough to do this he should not make analyses or publish or use his results, but should turn to other work. Such ethical considerations also bar out any such forms of dishonesty as "cooking" or "doctoring" analyses, a matter that is discussed later (p. 27).

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[1] Many an improvement in analytical methods has been suggested by an analyst who *thought about what he was doing* while engaged in routine work.

[2] Fresenius–Cohn, **1**, p. 4.

It may be said that the analysis of rocks (and silicate minerals) would seem to be especially suitable for women; whose characteristics of neatness, patience, application, care, conscientiousness, and attention to detail are essential to good analytical work. The author knows of five women who have made many rock analyses, and has found the work of all of them to be uniformly good.[1]

Completeness of Analyses.—The ideal analysis should show the percentage of every constituent in the rock as well as the absence of those the presence of which might be expected. This ideal is not always attainable, and for practical purposes an analysis should give figures for all constituents that are present in sufficient amount to make their determination a matter of interest, or the presence or absence of which may bear on the problem.

The number of constituents determined depends very largely on the character of the rock. Thus, in analyzing a granite, quartz-porphyry, or rhyolite, which are of simple composition and highly silicious, comparatively few constituents need be determined to make the analysis satisfactory. On the other hand, in such rocks as nephelite syenite, diorite, basalt, and tephrite, the number of constituents that may be present and should be determined is larger, and may reach twenty or more.

Neglect to seek for some of the rarer constituents may lead one to overlook important features, and an analysis complete as to the subsidiary constituents may be of great value in the future or to others, even if this degree of completeness is not necessary for the end immediately in view. The analyst should turn out, and the petrographer or petrologist should be willing to accept, only results of high or the highest character; so that it follows, as a general thing, that an analysis should be as complete as it is possible to make it. On the other hand, the making of a very complete analysis takes much more time than does one in which only the chief constituents

[1] These are M. W. Adams of New York, Laura Hezner of Zürich, Mary G. Keyes of Washington (D. C.), Naima Sahlbom of Stockholm, and Helen E. Vassar of Cambridge, Massachusetts. Cf. Washington, Prof. Paper **99**, p. 23.

are determined. The decision as to the course to be followed depends on the purpose for which the analysis is made, and on other circumstances.

The details of the constituents to be determined will be taken up later (p. 12 ff.), but it may be stated here that *all the major constituents must be determined in every analysis,* as well as those minor ones that enter into the composition of minerals that are present in notable amount. If the general character of the petrographic province or the microscopic examination indicates the probable presence of certain of the rarer elements, these also should be looked for.

3. MICROSCOPIC EXAMINATION[1]

Every chemical analysis of a rock should be preceded by a microscopic examination of a thin section of the rock specimen by a petrographer. There are several reasons for this. In the first place, by comparison of several specimens in thin section one is able to judge, better than by a merely megascopic examination, whether the specimen selected for analysis may be considered as really representative. It has happened more than once that specimens selected for analysis without microscopic study have been shown later to be abnormal forms and not typical of the rock-mass or volcano under investigation; or in other cases that several analyses have been made of one kind of rock, while equally important kinds have not been analyzed.

The microscope also frequently gives important indications as to the presence of important or rare constituents which should be determined, or the absence of others which may therefore be neglected. It will thus often prevent the overlooking of constituents the determination of which may be of considerable importance; or, on the other hand, may save the analyst's time and labor in searching for substances that are not present, at least in determinable amount.

Thus, if many microscopic zircons are present in a granite, the amount of zirconia should be determined to render the analysis satisfactorily complete, but if these are absent this substance may be neglected without serious diminution of the value of the analysis. The presence of crystals of a colorless, isotropic mineral of low refractive index will necessitate the determination of Cl and SO_3 as they may be colorless sodalite or haüyne, whereas if none are found under the microscope in a holocrystalline rock, Cl and SO_3 may often be considered as absent.

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[1] Cf. Hillebrand, Bull. **700**, p. 24; Washington, Prof. Paper **99**, p. 13; A. Holmes, Petrographic Methods and Calculations, 1921, p. 387; Hillebrand–Lundell, p. 651.

Finally, the thin section will often show more definitely than the hand-specimen whether the rock is not fresh or is so altered that analysis of it is not justified.

The percentage amount of certain constituents may be determined by the microscope in some cases with almost as much accuracy as by chemical analysis, and with greater ease and expedition. This is true of some that are present in very small amounts and occur in minerals of definite composition.

Thus, if zirconia is present only in zircon, or fluorine only in fluorite, or sulphur in pyrite, the amount of these minerals in the rock can be estimated by Rosiwal's method,[1] and the percentages of ZrO_2, F, or S, respectively, may thus be calculated. Even though this method also applies to phosphorus pentoxide in apatite,[2] this oxide is of such importance, and its determination analytically is so easy and expeditious, that its percentage should always be ascertained in the regular analytical way. This microscopical method is, however, less satisfactory than the chemical, and if it is adopted a note to that effect should be made in the statement of the analysis.

4. Constituents to be Determined[3]

Importance of Completeness.—In the earlier days of petrography, the petrographer was quite content if the analyst reported figures for only eight or nine constituents, and he did not always insist on the separate determination of the two oxides of iron. One seldom meets with analyses of that earlier period in which TiO_2 or P_2O_5 are mentioned, to say nothing of such constituents as ZrO_2, BaO, or F. In the absence of exact knowledge of the mineral composition of rocks the presence of such rare elements was not often suspected, nor did neglect of some of them in the course of the analysis necessarily cause such low summations as to give rise to the suspicion that something had been overlooked. This was partly because these rarer elements almost invariably occur in very small amounts, partly because some of them are precipitated and weighed with other constituents, and partly because the methods of analysis in those days were not as accurate as at present, and the analyst was content with a summation which would lead a modern chemist to reject or to repeat the analysis.

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[1] Rosiwal, Verh. Wien. Geol. Reich-Anst., **32**, 1891, p. 143; Cf. Cross, Iddings, Pirsson, and Washington, Quant. Class. Igneous Rocks, Chicago, 1903, p. 204; A. Holmes, Petrographic Methods and Calculations, 1921, pp. 313–325.

[2] As most apatites are fluor-apatite the amount of fluorine may be calculated (with fair safety) from that of the P_2O_5. It must be remembered that in certain regions (as in Norway) the apatite is chiefly a chlor-apatite.

[3] Hillebrand, Bull. **700**, pp. 18–30; Hillebrand–Lundell, pp. 645–653.

After it became possible to study rocks in thin section, and when the use of heavy solutions made the separation of the component minerals easy, it was found that the number of chemical constituents commonly present in rocks was far larger than had been supposed, although the importance of detecting them was not recognized for many years. With improvements in old methods and the adoption of new ones, the determination of these minor constituents was greatly facilitated, and at the present day analyses in which figures are reported for twenty or more constituents are common, at least in some countries; though, unfortunately, there is still some tendency among many chemists to rest content with the determination of only the more important ingredients.

Hillebrand[1] was the first to urge greater completeness in chemical rock-analysis. He himself practiced what he preached, and thus led the way and set the pace for the present-day complete analyses.

At first sight it may not seem worth while to pay attention to constituents that are present in amounts only up to a few tenths of one per cent. But there are very good reasons for not neglecting them.

For one thing, the determination or non-determination of some of them affects, and in some cases affects seriously, the figures for other and more important constituents. This is because several of them are precipitated and weighed together, and then all except one are determined separately, so that the figure for the final one depends on those of the others, since it is determined by difference.

Thus, Al_2O_3, Fe_2O_3, Cr_2O_3, V_2O_3, TiO_2, ZrO_2, P_2O_5, MnO, and a little SiO_2 are thrown down and weighed together, all except the first are determined separately, and the weight of the Al_2O_3, which is usually greater than all the others combined, is ascertained from the difference. It is evident that if any one of the other oxides is neglected the figure for alumina will be by so much too high, and this error may be serious. Similar cases are those of CaO and SrO, and of P_2O_5 and V_2O_5, though in these the error involved will rarely be of moment.

Again, the non-determination of those constituents which are not precipitated and weighed with others, lowers the summation of the analysis. This lowering may amount to so much as to cause an otherwise superior analysis to appear to be inferior.[1] Such non-determinations are those of H_2O, CO_2, SO_3, Cl, S, BaO, NiO, and in some cases MnO.

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[1] Hillebrand, Jour. Am. Chem. Soc., **16**, p. 90, 1894.

Another and even more important reason for completeness is that evidence is accumulating, as analyses of a high degree of completeness become more common, that much light may be thrown upon petrological problems of great theoretical interest by a knowledge of the presence of the rare elements. The subject has been discussed by Hillebrand,[2] whose strong plea for completeness it will be well for the student to read. A few illustrations may be given here.

The analyses of the U. S. Geological Survey show that baria and strontia are almost invariably present in igneous rocks of the United States, and that the former is in uniformly greater amount than the latter. Furthermore, it is made clear that, while never present in large amount, both of them are more abundant in the rocks of the Rocky Mountain region than in those to the east and west of it.[3] As Hillebrand says: "surely this concentration of certain elements in certain geographical zones has a significance which future geologist will be able to interpret, if those of today are not."

Similarly, we now know, through the complete analyses first used by the chemists of the U. S. Geological Survey, that titanium is not the rare element it was formerly believed to be, but that it is *ninth* in order of abundance of the elements that make up the known crust of the earth, being present to the amount of more than one-half of one per cent.[4]

Another important result of the determination of the rarer elements is the discovery that some of them are associated more especially with magmas of certain characters, but are seldom found in rocks derived from magmas of other chemical types.[5] Thus, it has been shown by Hillebrand[6] that vanadium is most abundant in rocks that are low in silica, while it is absent, or nearly so, in the highly siliceous rocks; conversely, molybdenum is confined apparently to the highly siliceous rocks.[1] It is now well known that high percentages of zirconium and of the rare earths are most frequently met in highly sodic rocks, whereas notable amounts of chromium and nickel are seldom met with in rocks that are not high in magnesia and iron and also low in silica and alkalies.

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[1] Cf. Washington, Prof. Paper **99**, p. 31.

[2] W. F. Hillebrand, Jour. Am. Chem. Soc., **16**, p. 90, 1894; Bull. **700**, pp. 18–24; Hillebrand–Lundell, pp. 645–652; H. S. Washington, Prof. Paper **99**, p. 16.

[3] Cf. Clarke and Washington, Prof. Paper **127**, pp. 47–49, 1924.

[4] Cf. F. W. Clarke, The Data of Geochemistry, U. S. Geol. Survey Bull. **770**, pp. 21, 29, 36, 1924; Clarke and Washington, Proc. Nat. Acad. Sci., **8**, p. 112, 1922; Clarke and Washington, U. S. Geol. Survey Prof. Paper **127**, pp. 5, 20, 38, 104, 1924.

[5] For a discussion of this subject and references see Washington, Trans. Am. Inst. Min. Eng., **30**, p. 735, 1908; Clarke and Washington, Prof. Paper **127**, pp. 102–107, 1924.

[6] Hillebrand, Bull. **700**, pp. 20, 21, 184; Hillebrand–Lundell, p. 352.

This leads to the consideration of a final point in favor of the present contention, namely, the light that may be thrown on the origin and formation of ores, and the possibility of such chemical study of the igneous and metamorphic rocks leading in the future to important economic advances in the indication of the possible existence of ore bodies.

The researches of Sandberger and others[2] have shown that many of the heavy metals, such as antimony, arsenic, bismuth, cobalt, copper, lead, nickel, silver, tin, and zinc, are present in the pyroxenes, hornblendes, biotites, and olivines of some igneous rocks, and can be detected if sufficiently large amounts are taken for analysis. Further consideration of this topic is uncalled for here, but from the point of view of the mining engineer and of geological surveys, it is clear that this is a weighty argument in favor of completeness and the determination of minor constituents in the making of chemical analyses of rocks.

Although it follows from the above that all rock analyses should be ideally as complete as it is possible to make them, yet the practical considerations of time and labor set limitations on this. Although by judicious management a number of the minor constituents can be determined along with the main ones, yet it is true that a thoroughly complete analysis will take a considerably longer time than a simple one. The analyst must judge for himself how far he can profitably go in this way, but it should be borne in mind that a few complete analyses will probably be of more value in the end than a larger number of incomplete ones.[3]

Although it is probable that all or nearly all of the known elements may occasionally be present in igneous rocks, and can be detected if sufficiently large amounts are taken for analysis, as Hillebrand has said, in practice we must, for the purpose of this volume, confine our attention to those which may reasonably be looked for in *silicate* igneous, metamorphic, and sedimentary rocks, and which may be readily determined in quantities of from one-half to two grams of material. Those, the determination of which will be considered in this book, are given in the following list, which is substantially that of Hillebrand:

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[1] Hillebrand, Bull. **700,** p. 23, 184; Hillebrand–Lundell, p. 245; Clarke and Washington, Prof. Paper **127,** p. 25.

[2] F. Sandberger, Zeits. Deutsch. Geol. Ges., **32,** p. 350, 1880; cf. J. H. L. Vogt, Zeits. Prakt. Geol., 1898, pp. 225 ff.; Clarke and Washington, Prof. Paper **127,** pp. 99 ff.; F. W. Clarke, U. S. Geol. Survey Bull. **770,** p. 640, 1924.

[3] See page 16 for a suggestion as to a practical procedure in regard to this.

SiO_2, TiO_2, ZrO_2, Al_2O_3, Fe_2O_3, Cr_2O_3, V_2O_3, $(Ce,Y)_2O_3$, FeO, MnO, NiO, CoO, MgO, CaO, SrO, BaO, BeO, CuO, Na_2O, K_2O, Li_2O, H_2O, CO_2, P_2O_5, F, Cl, SO_3, S, B_2O_3.

In addition, some elements of rare occurrence in igneous rocks, as lead, molybdenum, tin, or zinc, may be present in determinable amount; but these occurrences are met with so seldom, and the determination of these constituents involves such complicated methods that they will not be considered in this book.

In the majority of rocks, the constituents of the list just given are by no means of equal importance, and it is customary to divide them into "major" and "minor" constituents.[1]

In previous editions of this book and in other publications, such as U. S. G. S. Professional Paper 99, the author has divided the rock constituents into the two groups of "main" or "major"[2] and "minor," following the suggestion made many years ago[3] as to the statement of rock analyses. According to this former grouping the "major" constituents were the oxides: SiO_2, Al_2O_3, Fe_2O_3, FeO, MgO, CaO, Na_2O, K_2O, and H_2O. The "minor" constituents included TiO_2, P_2O_5, and MnO, as well as ZrO_2, BaO, S, etc. Present consideration, however, leads the author to make a *change in this arrangement.* This is to consider TiO_2, P_2O_5, and MnO, as "major" constituents,[4] instead of "minor" ones.

The division here adopted is: Major constituents, SiO_2, TiO_2, Al_2O_3, Fe_2O_3, FeO, MnO, MgO, CaO, Na_2O, K_2O, $H_2O\pm$, and P_2O_5; minor constituents, CO_2, $(Ce, Y)_2O_3$, Cr_2O_3, V_2O_3, NiO, CoO, BaO, SrO, BeO, CuO, F, Cl, SO_3, S, and B_2O_3.

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[1] Cf. Washington, Prof. Paper **99**, p. 15.

[2] The term "major" is now used instead of "main." Cf. A. Holmes, Petrographic Methods and Calculations, 1921, p. 385. "Major" is used also by Hillebrand–Lundell.

[3] H. S. Washington, Am. Jour. Sci., **10**, p. 61, 1900.

[4] The suggestion of naming these "sub-major" was considered, but was rejected as being an ultra-refinement.

The chief reason for this change is that two of the oxides, TiO_2 and P_2O_5, are invariably present in igneous rocks, the amount of TiO_2 being several per cent in many basalts and other femic rocks. Another reason is that TiO_2 and P_2O_5 are precipitated and weighed with the alumina, so that their weights must be subtracted from that of the mixed precipitate to arrive at the correct figure for Al_2O_3. Therefore, both of them must be determined to justify the ratings of "excellent" (first rate) or "good" (second rate).[1] MnO is placed with these because its determination is necessary (or at least advisable) to justify the rating "excellent," and advisable for that of "good," and because manganese is present in practically all igneous rocks, although its percentage is always small.

A further justification for considering TiO_2, P_2O_5, and MnO as major, rather than as minor constituents, is that these (now reckoned as major) are among the twelve most abundant *oxides* in the earth's crust. According to the latest estimate of the average composition of igneous rocks,[2] TiO_2 is the tenth, P_2O_5 is the eleventh, and MnO is the twelfth oxide in order of abundance; while titanium is the ninth, phosphorus the tenth, hydrogen the eleventh, and manganese the twelfth *element*.[3]

It will be noticed that this is essentially the grouping adopted with all the analyses (both "superior" and "inferior") collected in the tables of Prof. Paper 99 (1917). In these TiO_2, P_2O_5, and MnO are placed on the left-hand page, following immediately after SiO_2 to H_2O-, and are thus separated from the other "minor" constituents, which appear together on the right-hand page.

In fact, these three constituents are determined so frequently in modern rock analyses as to make this change advisable.

Major Constituents.—The new list of major constituents is, therefore: SiO_2, TiO_2, Al_2O_3, Fe_2O_3, FeO, MnO, MgO, CaO, Na_2O, K_2O, H_2O+, H_2O-, P_2O_5.

These thirteen[4] (including both oxides of iron) are invariably present in greater or less amount in all igneous and metamorphic silicate rocks, and all of them, (with the possible exception of MnO), must be determined in every rock analysis if it is to conform to the requirements as to satisfactory completeness.

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[1] Cf. Washington, Prof. Paper **99**, p. 25.

[2] Clarke and Washington, Prof. Paper **127**, p. 16, 1924.

[3] Clarke and Washington, *op. cit.*, p. 20.

[4] H_2O- is, properly, a minor constituent, but it is inadvisable to separate it from H_2O+.

The only exceptions would be certain rare types, with which the student is not likely to meet. Thus, the amount of alkalies in dunite is so small as to be negligible for most purposes. But even in such rocks it is far better to prove definitely that these constituents are either absent or present, even if only in traces. In the light of physico-chemical investigation of solutions, this knowledge may be of interest and importance in the future, as applied to rock magmas.

Stress must be laid on the importance of the *separate determination of both oxides of iron,* which have been only too often not separately determined but reported in the analysis as either Fe_2O_3 or FeO. Neglect of this point was especially common up to forty years ago, and is the cause of the relative worthlessness of many of the older analyses.[1]

Inasmuch as the two oxides of iron play different rôles in the composition of minerals, a knowledge of the relative amounts of each is necessary for a proper understanding of the rock magma, the calculation of the mode (actual mineral composition) of the rock, or for its classification along chemico-mineral lines. Although the error involved by their non-separation may be small in certain highly quartzose or feldspathic rocks, as granites, rhyolites, trachytes, and syenites, in which they do not amount together to more than one or two per cent, yet the conscientious analyst should always make it a point to determine them separately.

As an illustration of its possible importance may be cited the observation that FeO is higher than Fe_2O_3 in glassy rhyolites, whereas Fe_2O_3 is higher than FeO in holocrystalline rhyolites of the same general composition and at the same volcano, the total amounts of both being less than two per cent. This led to the discovery that the same relation holds good generally for basalts and for many other kinds of lava.[2]

Water is often present in notable amount, and therefore it is to be reported in every rock analysis, even though the amount of water is not vital to our knowledge of the rock, except when minerals containing water of crystallization or hydroxyl, such as analcite and micas, are present. The determination of water is also important because it gives a measure of the freshness of the rock. There is all the more reason for doing this because the determinations of both H_2O+ and H_2O- are easy and take little time, and because the neglect to determine water may seriously affect the summation of

[1] Cf. Washington, Prof. Paper **99**, pp. 15, 21, 26.

[2] H. S. Washington, Am. Jour. Sci., **50**, p. 458, 1920.

the analysis.[1] It is also evident that the determination is essential in the investigation of many metamorphic and sedimentary rocks, and in the study of rock weathering and alteration, where hydrous minerals, as chlorite, zeolites, and limonite, are present.

Water may be present as either or both "hygroscopic" (H_2O —) and "combined" (H_2O+) water, which are expelled from the rock powder at temperatures respectively below and above 105°–110°, the latter being the conventional temperature. There is difference of opinion as to the advisability of determining them separately, as well as reporting the hygroscopic water in the analysis. The arguments for and against their separation have been discussed by Hillebrand,[2] and need not be repeated here. Although the matter is not of great importance, it may suffice to say that the author concurs with the opinion of Hillebrand in recommending their separate determination and inclusion in the statement of the analysis, and also in the use of air-dried material for analysis.

The case of manganous oxide is more complex, and for its discussion we must anticipate some of the features of the analysis. If the alumina is precipitated with ammonia alone, as is usually done, some of the manganese comes down with the alumina. A little of it comes down later with the lime, and the rest falls with the magnesia.[3]

It is clear, therefore, that unless the manganous oxide is completely separated from the alumina, and if it is not precipitated before the determination of lime and magnesia, it will be distributed among these three constituents.

On the other hand, while it may be completely separated from the alumina by what is known as the "basic acetate" method, and then precipitated as sulphide before lime and magnesia are determined, yet this procedure is liable, as we shall see (pp. 167, 175), to cause serious errors in the determination of alumina and iron oxides; likewise it is tedious and involves at least one day's extra time.

Fortunately, manganous oxide is present in very few rocks in amounts greater than two or three tenths of one per cent, so that even if it is neglected and its weight is distributed among alumina, lime, and magnesia, the error will not usually be serious and may be disregarded as being negligible.

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[1] H_2O is the ninth oxide in order of abundance in the igneous rocks.

[2] Hillebrand, Bull. **700**, p. 72; Hillebrand–Lundell, p. 684.

[3] The distribution of manganese has been studied by G. Steiger, in the U. S. Geological Survey Laboratory. Cf. Hillebrand, Bull. **700**, p. 134; Hillebrand–Lundell, p. 741; Mellor, p. 371.

Manganous oxide can, however, be thrown down with the alumina by bromine or ammonium persulphate, so that it will not subsequently affect the figures for lime and magnesia. It is determined in a separate portion by a colorimetric method, and its weight is then to be subtracted from that of alumina. This is the best procedure in the majority of rock analyses, and we can say that manganous oxide should always be determined colorimetrically, although it need not be separated from the other important constituents if its amount is very small.

Besides the constituents discussed above, there are a number that occur, generally in small amount, but that in some rocks may assume equal importance with, or may even surpass, some of the major constituents enumerated above. There are few examples of this, but their number is rapidly growing with increase in our knowledge of the less well-known rocks of the globe, and many of them are of special interest from the theoretical side. As illustrations there may be cited titaniferous ores produced by differentiation, as those of the Adirondacks; the apatite-rich and ilmenite-rich nelsonites of Virginia; such sodalite- and haüyne-rich rocks as tawite, taimyrite, and haüynophyre; the eudialyte-rich lujavrites of Kola and Greenland; and the apparently igneous pyritiferous ores of Norway. In these, certain constituents that are usually regarded as minor, Cl, SO_3, ZrO_2, and S, respectively, as well as TiO_2 and P_2O_5, assume an importance which is equal to that of some of the twelve mentioned above, so that it is clear that an analysis of such rocks which does not take these usually minor constituents into account is seriously defective.

Minor Constituents.—According to the grouping here adopted the minor constituents include: CO_2, $(Ce, Y)_2O_3$, Cr_2O_3, V_2O_3, NiO, CoO, BaO, SrO, BeO, Li_2O, F, Cl, SO_3, S, and B_2O_3.

The determination of these differs much in their relations to the completeness of the analysis. Some are precipitated and weighed with major constituents and their weight is afterward to be subtracted from that of the mixed precipitate. Therefore, if they are not determined the apparent amount of the major constituent, which is determined by difference, will be too great. This is true, for instance, of the oxides of zirconium, chromium, vanadium, and the rare earth metals. All these are precipitated and weighed with the alumina, and if they are not determined the weight of the alumina will be increased by their combined weight. As these oxides are each seldom present in amount greater than a few tenths of one per cent, and usually much less, neglect of them will seldom involve appreciable error in the figure for alumina.

Zirconia is apt to occur in notable, though small, amounts in rocks that are high in soda, so that it is well to determine zirconia in such rocks; and chromium sesquioxide and vanadium sesquioxide[1] may be determined in rocks that are high in magnesia and iron and low in silica.

Analogous cases are strontia and lithia. The first of these is precipitated and weighed with the lime, and is afterward separated from it to arrive at the true weight of the lime. Similarly, lithia is weighed with soda, thus increasing its apparent amount. But both strontia and lithia (especially the latter) are present in such minute amounts that their non-determination will seldom affect the figures for lime or soda to an appreciable extent. They are chiefly of interest from the theoretical side, and this applies more especially to strontia.

The second group of minor constituents consists of those, the determination of which does not affect the figures for any of the major constituents. These include nickel, cobalt, copper, and barium oxides, sulphur, sulphur trioxide, chlorine, fluorine, and carbon dioxide.

Of these the first three occur as a rule only in traces in igneous rocks, nickel more abundantly in the less siliceous ones, in which it may be well to determine it. Indeed the determination of nickel is advisable in very particular analyses of intermediate to basic rocks. It is always necessary in analyzing meteorites, though neglect of it will seldom if ever lead to serious error in dealing with terrestrial rocks. Copper cannot be considered an important constituent, but it may well be looked for in rocks low in silica, as it may be of theoretical interest.

As has been mentioned above (p. 9), baria is a constant constituent of the igneous rocks of the United States, and it is almost certain that it will be found to be widely distributed elsewhere when it is looked for systematically. In view of its theoretical interest and the comparative ease of its determination by the method given beyond, it will usually be advisable to look for it in the course of the analysis.

Sulphur is sometimes present as the sulphides pyrite and pyrrhotite, and indeed more often than was formerly believed, especially in the less siliceous rocks. Its amount can be readily ascertained along with that of the baria, and it (or SO_3) should enter into the statement of most analyses or its absence be definitely shown.[1]

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[1] Vanadium sesquioxide is also precipitated and weighed with the phosphorus pentoxide, so that its amount should be subtracted from that of the latter. See page 246.

Sulphur trioxide and chlorine are met with in igneous rocks rather frequently, especially in rocks that are high in soda, and both are always to be determined if minerals of the sodalite group are present. It is always well to determine them in rocks liable to carry such minerals, even if these are not visible with the microscope. In other rocks (especially lavas) it can scarcely be held to be a great loss of time to look for them, in view of their probable theoretical interest and the ease of their determination.

Fluorine is seldom present in quantities of over a few tenths of one per cent and need seldom be looked for. This may be done, however, if the rock contains fluorine-bearing minerals, but even here its determination is necessary only if these are abundant or for very accurate work. Neglect of fluorine is the more excusable because of the probable inaccuracy of the determination.

Carbon dioxide is often present in igneous and metamorphic silicate rocks, but, as far as is now known with certainty, only when the rock is altered, as a component of secondary minerals, calcite, dolomite, siderite, and cancrinite. If it is present it should be determined, because it serves to a certain extent as a measure of the freshness of the rock, and because the result may have a bearing on the problem of the occurrence of calcite or cancrinite as a primary constituent.

It is to be remembered that if water is determined as "loss on ignition," this will include the carbon dioxide, which is also expelled. The latter must, therefore, be determined separately and directly.

As a final and practical solution of the difficulty in deciding what constituents to determine the following procedure is suggested.[2] If only one or two rocks are to be analyzed, especially if they come from a little-known locality, the analysis should be as complete as time and other considerations permit. But if a series of analyses is to be made of the rocks of a region or volcano that includes various types, two analyses should be made of each of the most important. All of these analyses should show the amounts of all the major constituents, including TiO_2, MnO, and P_2O_5, and of the usually minor ones which may be of major importance. The rarer constituents, such as ZrO_2,

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[1] In the case of basalts and other rocks known to contain none of the sodalite minerals the author's present practice is to enter all sulphur as S in the statement of the analysis.

[2] Cf. Washington, Prof. Paper 99, p. 17.

Cr_2O_3, BaO, NiO, Cl, and S, need be determined in only one each of the more important types. This may be regarded as the optimal compromise between the ideal and the practical.

5. The Occurrence of the Various Elements[1]

The increased number of analyses of igneous rocks, and the more frequent determination of the minor constituents, with the many data obtained by the use of the microscope, have shown that certain of the rarer elements are prone to occur in rocks of certain chemical characters. Although our knowledge along this line is far from complete, a few words may be devoted to this subject, as it will often be of use to the analyst to know which elements should be determined and which may safely be neglected. Some of the various minerals that carry the several elements in question will also be mentioned, as well as the amounts in which the elements occur in igneous rocks.

Titanium is invariably present in igneous rocks, as shown by all analyses in which it has been sought for, and it is ninth in order of abundance among the elements that make up the crust of the earth. Titanium shows a decided preference for sodium rather than for potassium, and for iron rather than for magnesium.[2] Its amount is small in the more quartzose and feldspathic rocks, but it is more abundant in the more femic (basic) rocks, amounts of from two to five per cent TiO_2 being found in many basalts.

TiO_2 is an essential component of ilmenite and of perofskite, which are most common in femic rocks, and of titanite, which occurs in rocks with more silica. The oxide rutile is rare in igneous rocks, but occurs in metamorphic schists and phyllites. Titanium is also present in some magnetite and hematite, and very commonly, but to a less extent, in pyroxenes, amphiboles, biotites, garnets, and other ferromagnesian minerals. The amount of TiO_2 in igneous rocks varies usually from tenths of one per cent to about two per cent, but it may be present in larger quantity, up to five or six per cent.

Zirconium is present in many rocks in small amount, and it probably occurs in most granites, rhyolites, syenites, trachytes, and especially in nephelite syenites, phonolites, and tinguaites. It is most abundant in rocks that are high in soda, such as the last three, but not so much so in sodic lavas that are also high in lime, as nephelite tephrite.[1] It is rarely met with in rocks that are high in lime, magnesia, and iron. Zirconium is usually found as the silicate zircon, especially in granites and syenites, but it is also an ingredient of some rare zirconosilicate minerals, such as eudialyte, lavenite, and rosenbuschite. It has been shown recently[2] that zirconia (with the rare earths) is present in acmite and acmitic pyroxenes. Zirconium is present usually in amounts of less than 0.20 per cent of ZrO_2, but it may rarely reach two per cent or more.

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[1] F. W. Clarke, Bull. U. S. Geol. Survey **78,** pp. 34–42, 1891; J. H. L. Vogt, Zeits. Prakt. Geol., pp. 225 ff., 1897; F. W. Clarke, Bull. U. S. Geol. Suvery **168,** pp. 13–16, 1900; Bull. U. S. Geol. Survey **616,** pp. 13, 39, 1916; J. F. Kemp, Ore Deposits of the United States, p. 35, New York, 1900; Hillebrand, Bull. **700,** pp. 25–30; H. S. Washington, Trans. Am. Inst. Min. Eng., **30,** p. 809, 1908; J. P. Iddings, Igneous Rocks, **1,** p. 27, 1909; Clarke and Washington, Prof. Paper **127,** pp. 99, 103–106, 1924; Washington, Prof. Paper **99,** p. 16, 1917; Behrend und Berg, Chemische Geologie, 1927, pp. 38–49.

[2] Clarke and Washington, Prof. Paper **127,** p. 104, 1924.

The *rare earths,* oxides of cerium and yttrium, and of their congeners, are found in notable amount, so far as known, only in rocks that are high in soda. They form part of allanite, a mineral that is rather widespread in granites, and also of monazite, mosandrite, xenotime, and other minerals of even greater rarity. They are almost always accompanied by notable amounts of zirconia, with which cerium, rather than yttrium, is more often associated. The rare earths, reckoned as $(Ce, Y)_2O_3$, are seldom present in more than one-tenth of one per cent, but a few rocks are known in which they are present to the extent of from 0.4 to 1.8 per cent. Scandium has been shown spectroscopically to be widespread in traces.

Chromium is confined almost wholly to the femic rocks, especially those that are high in magnesia and low in silica, which consequently contain abundant olivine, such as peridotite and dunite. It occurs as the minerals chromite and picotite (chrome-spinel) and in a few augites, biotites, and olivines. It may occur up to one-half of one per cent of Cr_2O_3.

Vanadium, according to the investigations of Hillebrand,[3] "predominates in the less siliceous igneous rocks and is absent, or nearly so, in those high in silica." It is an ingredient of pyroxenes, hornblendes, and biotites, but not of olivine, and is also present in the ilmenite of some titaniferous ores. The amount of vanadium is always very small, seldom over 0.05 per cent of V_2O_3.[4]

[1] Clarke and Washington, Prof. Paper **127**, p. 104.

[2] Washington and Merwin, Am. Mineralogist, **12**, p. 233, 1927.

[3] W. F. Hillebrand, Am. Jour. Sci., **6**, p. 209, 1898. A. A. Hayes (Am. Jour. Sci. (3), **10**, p. 61, 1875) had shown that vanadium is present in many rocks: this was known by Hillebrand.

[4] Dr. Hillebrand laid what seems to the author to be undue stress on the vanadium content of igneous rocks and its importance for the analysis.

Manganese is uniformly present in nearly all rocks, but its amount is small, usually in tenths of one per cent as MnO, being only very exceptionally one-half of one per cent or more. The high figures often reported are, in most cases, regarded by the author as due to analytical error, an opinion in which Dr. Hillebrand concurred. Manganese is present in the ferromagnesian minerals, pyroxenes, amphiboles, micas, olivines, and garnets, and therefore is usually present in greater amount in the more femic (basic) rocks. It seems to favor rocks high in iron rather than those high in magnesia.

Nickel and Cobalt, like chromium, are most abundant in olivine rocks, but nickel oxide has been determined in some basalts. Both elements are constantly present, often abundantly, in meteorites. Nickel and cobalt occur as ingredients of olivine, as well as in pyrite and pyrrhotite, and in hornblendes and biotite to a small extent. An alloy of iron with nickel occurs rarely in basalts, but is very abundant in meteorites. The amount of nickel in terrestrial rocks is seldom more than 0.50 or 0.10 per cent; and the amount of cobalt is invariably less than that of nickel and seldom is more than a trace. In meteorites also the amount of nickel is always much greater than that of cobalt. In some analyses nickel has undoubtedly been reported too high, probably having been confounded with contaminating platinum.

Copper is to be found in many igneous rocks, but as a rule merely in traces. It is probable that the copper reported in some analyses of igneous rocks is really platinum derived from the platinum basin and crucibles, while again it may be due to contamination from the copper water-baths, etc. Copper is most frequent in the more femic (basic) rocks, such as gabbro, diabase, and basalt, entering the pyroxene and amphibole. It is an essential component of chalcopyrite, and is present in traces in some pyrite. Copper also (rarely) occurs as the metal in basaltic rocks.

Barium and Strontium[1] are present in most igneous rocks, the latter invariably in less amount than the former. There is much evidence that barium is most abundant in rocks that are high in potash. Barium occurs in the feldspars, especially orthoclase (in the celsian molecule), in the rare hyalophane, in some zeolites, as well as in a few biotites and muscovites. We can, at present, form no definite conclusion as to the character of the rocks most likely to carry strontium, and more analytical data on this point would be of interest. The amount of BaO may reach one per cent, though it is usually in tenths of a per cent, while that of SrO is little more than a trace, as a rule, but may exceptionally run up to 0.30 per cent.

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[1] Cf. W. F. Hillebrand, Jour. Am. Chem. Soc., **16**, p. 81, 1894; Clarke and Washington, Prof. Paper **127**, p. 103.

Lithium[1] is an element of very widespread occurrence, but it is seldom met with in rocks in more than spectroscopic traces. It is most abundant in highly alkalic rocks, and there is good reason to believe that it is especially prone to occur in those that are sodic, rather than potassic. Apart from the occurrence of lithium as an essential constituent of such minerals as lepidolite and spodumene, which occur in highly silicic pegmatites and granites, it is to be found in the alkali feldspars, muscovite (not in biotite), beryl, tourmaline, and other silicate minerals.

Phosphorus is almost invariably present in igneous and metamorphic rocks, as is titanium, and like this element it is most abundant in the more femic ones, especially in those that are high in lime and iron rather than in magnesia. It occurs almost solely in apatite, or very exceptionally as monazite or xenotime. The quantity of P_2O_5 usually runs from 0.10 to 1.00 per cent, generally much under the latter figure, but it may occasionally amount to several per cent.

Sulphur, as sulphides, is far more abundant in the femic rocks of all kinds than in the salic ones. It forms an essential ingredient of pyrite and pyrrhotite. These two sulphides are present in some plutonic igneous rocks, especially the basic ones (gabbro, etc.) ; more rarely in the lavas, such as diabase and basalt. In these last, especially, their amount is usually very small, and most of these rocks contain none of these minerals. They are more apt to occur in the metamorphic schists. As regards igneous rocks in general the author thinks that Dr. Hillebrand attributed too great importance to the presence of pyrite and pyrrhotite, especially as to their influence on the determination of iron oxides. As the trioxide (SO_3) sulphur occurs in the minerals haüyne, nosean, and lazurite; usually in the less siliceous rocks, though some haüyne rocks carrying quartz are known. These three minerals are most apt to occur in rocks that are high in soda. Sulphur, as sulphides, is present usually in tenths of a per cent, as is also true of SO_3, though in some rocks the amount may be much higher. Sulphur is often reported as SO_3, instead of as S, although its condition is not known. This is inadvisable.

Chlorine is present most abundantly in rocks that are high in soda, and especially when so low in silica that nephelite is present, though it is also found in nephelite-free rocks, and in a few that are quartz-bearing. It is an essential component of sodalite and nosean, and it is also present in some scapolite and in a few apatites. It also occurs, as sodium chloride, in liquid inclusions. The amount of chlorine is usually a few tenths of one per cent, but in sodalite rocks it may be one per cent or more.

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[1] Cf. Clarke and Washington, Prof. Paper **127**, p. 102.

In specimens of rocks collected near the sea-coast the presence of chlorine may be due to contamination by sea-water. This should be ascertained and determined by leaching the rock powder (p. 262).

Fluorine, as a component of apatite, biotite, hornblende, etc., seems to have no special preference as to magma, though, on the whole, it is found more frequently in silicic than in femic rocks. It is, however, to be met with as fluorite and some rare fluosilicate minerals, in highly sodic rocks that contain nephelite, such as nephelite syenite and tinguaite.[1] It is an essential constituent of fluorite and of most apatite, and as an integral part of the last mineral fluorine is ubiquitously present. Fluorine also occurs in small amount in biotite and other micas, in some hornblende, as well as in tourmaline, topaz, chondrodite, vesuvianite, apophyllite, etc. The usual amount of fluorine is very small, generally from traces to 0.10 per cent, only rarely being above the latter figure.

Beryllia has never, so far as I know, been determined in the analysis of any igneous rock. Yet the fact that the aluminosilicate, beryl, is not a rare mineral indicates that beryllium is fairly widespread.[2] Beryl occurs in granitic and syenitic pegmatites, especially sodic ones. It is also found in metamorphic rocks. It has been suggested[3] that in some cases beryllia has been weighed with, and supposed to be alumina, unidentified beryl being present, thus accounting for an apparent excess of Al_2O_3, which it is difficult to reconcile with the mineral composition of the rock. It has been shown recently that alumina has been mistaken for beryllia in the mineral vesuvianite,[4] in which the presence of beryllium had not been suspected. The need of a closer study of some minerals and rocks as regards this point is obvious. It might be well to determine BeO in granites associated with beryl-bearing pegmatites and in some nephelite syenites.

Tin, as the oxide cassiterite, is confined to the highly silicic rocks, granites and pegmatites, and its presence is due generally to pneumatolytic processes. It may also occur in traces in ilmenite, micas and feldspars.

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[1] Cf. Clarke and Washington, Prof. Paper **127**, p. 105.

[2] Clarke and Washington, Prof. Paper **127**, pp. 25, 103, 1924.

[3] H. S. Washington, Trans. Am. Inst. Min. Eng., **39**, p. 753, 1909.

[4] Palache and Bauer, Am. Mineralogist, **15**, p. 30, 1930.

Thorium seems to be most abundant in highly sodic rocks.

Radium, however, shows a preference for potassium rather than for sodium,[1] as is true of the related barium.

Molybdenum, tungsten, and uranium are confined almost exclusively to very siliceous rocks.

Zinc has been met with in granites, as well as in basic rocks, but no generalization in regard to it is possible as yet.

Platinum is found almost exclusively in peridotites, but is occasionally met with in connection with gabbros.

Boron, as a constituent of tourmaline, is most apt to occur in highly siliceous granites, but the frequent occurrence of the borosilicate, datolite, as a secondary mineral with basaltic rocks, indicates that it is more abundant than is generally thought.[2]

6. Statement of Analyses

The results of the analysis might be stated in terms either of the elements present or of the basic oxides and acid radicals.[3] Though the former may be the more logical on purely theoretical grounds, yet the latter greatly facilitates calculations based on the analytical data, and being universally in use, renders comparison of all rock analyses with each other very simple. It is therefore to be adopted without question.

Many years ago it was proposed[4] that petrographers and chemists follow a uniform order in the statement of the analyses of rocks. This was adopted in its esentials by the chemists of the U. S. Geological Survey, and has been used by most petrographers for many years. Until recently there has been no cogent reason for modifying it, but the addition of TiO_2, MnO, and P_2O_5 to the number of major constituents, adopted here, necessitates a change in the order of oxides in the statement of analyses. The order of statement here adopted is:

SiO_2, TiO_2, Al_2O_3, Fe_2O_3, FeO, MnO, MgO, CaO, Na_2O, K_2O,

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[1] Cf. A. Holmes, Geol. Mag. (6), **2**, p. 63, 1915; Joly, Phil. Mag., **18**, p. 577, 1909; Joly, idem, **24**, p. 697, 1912; Clarke and Washington, Prof. Paper **127**, p. 103, 1924.

[2] Cf. Clarke and Washington, Prof. Paper **127**, p. 25.

[3] Cf. Hillebrand, Bull. **700**, p. 31; Hillebrand–Lundell, p. 658; Mellor, p. 251; Ostwald, pp. 212–215; A. Holmes, Petrographic Methods and Calculations, 1921, p. 389.

[4] H. S. Washington, Am. Jour. Sci., **10**, p. 59, 1900.

P_2O_5, H_2O+ (>110°), H_2O- (<110°), CO_2, ZrO_2, F, Cl, SO_3, S,[1] $(Ce, Y)_2O_3$, Cr_2O_3, V_2O_3, NiO, CoO, BaO, SrO, BeO, CuO, Li_2O, B_2O_3.

By putting the twelve major oxides together and in the first section, the general character of the rock may be seen at a glance. Furthermore, whether an analysis is complete or incomplete as to the minor constituents, the twelve major oxides are always in the same relative positions, thus greatly facilitating comparison with other analyses.

This order has been used in recent papers by Daly, Tyrrell, and by other petrologists, except that P_2O_5 follows H_2O (+ and —) and precedes CO_2.[2]

As regards the *major constituents,* we begin with the two chief acidic dioxides, the first (SiO_2) being that which is always present in largest amounts, TiO_2 following immediately after SiO_2. We then pass through successively lower orders of oxides to the most positive bases, the alkalies. At the same time, these are presented in an order that brings most of the oxides together in their natural mineral and petrographic relations.

Alumina, which is amphoteric, and is usually the most abundant constituent next to silica, follows immediately after this (and TiO_2), and is succeeded by the other major sesquioxide, Fe_2O_3. Ferrous oxide follows ferric, and next comes manganous oxide (MnO), which replaces FeO in many minerals. Magnesia comes next, as MgO and FeO go hand in hand in the ferromagnesian minerals. Lime follows, in an intermediate position between magnesia and the alkalies, because it enters prominently into the ferromagnesian minerals and the lime-soda feldspars. Soda precedes potash, because it is associated with lime in the plagioclases. Phosphorus pentoxide comes next, as being more important than H_2O. Water follows immediately after, since it is an important and always determined constituent. Combined water precedes hygroscopic water,[3] as the more important and because it is present almost without exception in greater amount than the latter. The two together (with CO_2) constitute the "loss on ignition" frequently given, and may then be connected by a bracket in tabular statements.

The *minor constituents* are more difficult to arrange in a logical sequence, but that adopted here seems to be the best compromise. The acidic radicals precede the basic oxides, as before.

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[1] FeS_2 is not to be used in the statement.

[2] G. W. Morey necessarily adopts a quite different order of statement in his Table of Glass Compositions (Int. Crit. Tables, **2**, 1927, pp. 89–91). Departures from this order are also necessary for many silicate minerals.

[3] In this respect the order of statement adopted by the U. S. Geological Survey differs from that suggested by the present author.

Carbon dioxide comes first, as it is a dioxide, and because it thus can be bracketed with H_2O as "loss on ignition." Zirconia follows, as it is an amphoteric dioxide, which forms zirconosilicate minerals. Next come the strongly negative fluorine and chlorine, the former preceding as being ubiquitously present in apatite, although not often determined. Sulphur trioxide and sulphur follow, the oxide preceding because it enters into the sodalite group of minerals, as does chlorine, while sulphur forms pyrite and pyrrhotite. These sulphides are occasionally secondary, so that in this respect sulphur corresponds to water and carbon dioxide. FeS_2 should not be used in the statement of analyses, because it is often not certain that the sulphur does not belong to pyrrhotite, and furthermore it thus represents a mineral, not a chemical constituent. In my most recent papers I have calculated and stated all sulphur, whether S or SO_3, as S, unless minerals of the sodalite group are definitely known to be present.

The subordinate oxides follow in the order R_2O_3, RO, and R_2O. Of the sesquioxides, those of the rare earth metals come first, because they are often analogous to or replace Al_2O_3 and Fe_2O_3 in silicate minerals. Chromium sesquioxide precedes that of vanadium because it is much more important and abundant and is more often determined. These two might be placed among the minor acid radicals, but the position here assigned to them seems better.

Nickel oxide is the first of the monoxides, because it is fairly common and is occasionally determined. Cobalt oxide, of course, is placed along with it. Baria and strontia follow nickel oxide, just as lime is placed after (Fe,Mn)O among the major constituents. Baria precedes strontia as the more abundant and important, and because it is more often determined. BeO may be inserted here, although it is rarely determined. The monoxide of copper (with that of zinc) is placed next, and lithia follows as the minor representative of the alkalies. Boron trioxide should logically be placed after zirconia, but it closes the list because it is rarely determined in igneous rocks.

In the statement of analyses the term "trace" is often used, to indicate that a constituent is present, or supposed to be present, in a small but undetermined amount. The usage of the term is loose, and in some cases quite erroneous, as more complete analyses have shown that such "traces" often amount in reality to one-half of one per cent, and frequently to several per cent. It would be better that the meaning of the term should be more strictly defined, and it has been suggested[1] that "trace" should "indicate strictly and uniformly that the constituent (to which it is applied) has been looked for and found, but in unweighable amount (0.1 milligram or less)." If there is no knowledge as to the presence of a constituent a dash (—) may be used. Hillebrand suggests: "In the tabulation of analyses a special note should be made of an intentional or accidental neglect to look for substances which it is known are likely to be present." For this purpose the letters "n.d." (not determined) may be reserved.[2] The absence of any constituent looked for should be stated in the tabulation[3] and not in the accompanying text, as is sometimes done, since the fact is thus apt to be overlooked.

The analytical calculations should be carried out to four decimals, so that in the statement of analyses the figures are given to hundredths of one per cent, that is, *to two decimal places of a per cent.* Although the last decimal is not of much significance, it represents the limit of weighing (0.0001 gram) in the quantities taken for the determination of the constituents of rocks, and gives some indication of the value of the preceding decimal. It is also the almost universal practice among chemists and analysts.[4] Statement in only tenths of a per cent is defective in that it implies correctness only in the unit column, and consequently an insufficient degree of accuracy for the minor constituents.

On the other hand, a statement in thousandths of a per cent (three decimals), implies a higher degree of accuracy than that found in all but the most painstaking analytical work, such as the determination of atomic weights. This is quite uncalled for in view of the variable composition of all rock masses from place to place, however great may be the apparent uniformity. In the course of compiling and examining thousands of rock analyses the author has found—really without exception—that the few analyses that are stated to thousands of a per cent (to three decimal places)[5] are remarkable chiefly for their poor quality, differing from the probable truth in some constituents by as much as one or more per cent. Statement in such ultra-refined terms is evidence that the analyst has no just appreciation of the probable limits of error or of the bases of accuracy in analytical work. It is safe to disregard an analysis that is stated to three or four decimals.

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[1] H. S. Washington, Prof. Paper **99**, p. 16. Cf. Hillebrand, Bull. **422**, p. 29.

[2] The letters "p.n.d." are used to denote that the substance is known to be present (as shown by the minerals in the rock), but that it has not been determined.

[3] The terms "none," "nil," or 0.00 may be used; the author's preference is for the first of these.

[4] This topic is well discussed by Mellor (p. 16), who says: "As a matter of fact, two decimals are generally used in technical analysis because we have grown accustomed to the plan, not because it represents the accuracy of the work."

[5] A few analyses are stated to four decimal places, and in some (stated to three decimals) the alkalies (not separated) are given as the difference from 100 per cent.

A few words must be said as to the recalculation of the analysis to an even 100 per cent. This is permissible, or may even be necessary, for such purposes as comparing rock analyses, especially if the figures for insignificant constituents are omitted.

But the student must adhere strictly and conscientiously to the rule that a defective analysis must never be "cooked" or "doctored." That is to say, if the summation of the analysis is decidedly high or low the excess or deficiency must not be distributed among the various constituents or the figures so altered or adjusted as to make the analysis sum up to almost or exactly 100 per cent.[1]

For one thing, as Hillebrand and Fresenius point out, any such excess or deficiency is not caused by errors in all the constituents, but the error is more than likely to affect a single constituent or several of them.

As Mellor says: "The practice of adjusting the results of an analysis to exactly 100 per cent is utterly bad." Ethically it is dishonest, the more to be shunned because the readjustment is not evident and can be detected only with difficulty, if at all.[2] Also, as Fresenius points out, "such 'doctoring' of the analysis deprives other chemists of the power of judging its accuracy."

Whatever the results of an analysis may be, and whether the summation is high or low, the figures for the various constituents should be given with their summation as they are obtained, if the analysis is deemed to be worthy of publication at all.

The student might well read the story of the courageous and candid publication by Plattner in 1846 of his analysis of pollucite, an aluminosilicate of caesium, although his summation was very low (92.753), because he mistook for potassium the then undiscovered caesium, which has a much higher atomic weight.[3] When it was recalculated on the proper basis it was found to be very satisfactory.

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[1] Fresenius–Cohn, **2,** p. 169; Hillebrand, Bull. **700,** p. 30; Hillebrand–Lundell, p. 654; Mellor, p. 246.

[2] The agreement of the analysis with the true chemical composition can in many cases be checked by the expert petrographer, especially if he is conversant with methods of analysis.

[3] Cf. S. L. Penfield, Am. Jour. Sci., **41,** p. 213, 1891; Mellor, Treatise Inorg. Chem., **2,** p. 427, 1923.

The recalculation of analyses of altered rocks to 100 per cent, to eliminate H_2O and CO_2, is also reprehensible, but on other grounds than that of dishonesty. It is discussed on page 76.

An analysis that foots up to exactly 100.00 is looked on with suspicion by some. This, however, is quite unjustifiable, and the figure is not evidence, in itself, of readjustment. The case occurs but seldom and is purely accidental. The determination of some of the undetermined minor constituents, such as BaO or S, which do not affect the percentages of other constituents, would add to the summation. On the other hand, a summation of 100 per cent (or close to it) is not conclusive evidence that the analysis is correct, although it is some check on the accuracy of the work.

PART II

APPARATUS AND REAGENTS

Although any well-equipped laboratory should have at hand every piece of apparatus and all the reagents that are necessary for the quantitative analysis of rocks, it may be convenient, especially for the independent worker, to give a list of those that should be available during the progress of a properly carried out analysis. The number of pieces of apparatus suggested comprises those which it is deemed advisable to have on hand, so that several operations may be made at the same time. The amounts of reagents are such as it will be well to provide when stocking up an individual laboratory.

Suggestions as to general laboratory equipment are not made, as such equipment is usually provided for the student and can seldom be radically changed. It may be well, however, to emphasize the importance of a hood with a good draft, provision of a water-bath, and efficient arrangements for keeping the laboratory clean and free from dust and fumes. The advisability of having the cocks and connections for gas, vacuum, and water in front of the work-bench, instead of at the back, must be stressed. (See frontispiece.)

An excellent material for the top of the work-bench and the shelves is the so-called "Alberene stone," a massive variety of steatite,[1] from Alberene, Virginia. There should be no streaks of calcite or pyrite. The shelf on which the acid reagent bottles are kept may be protected by thin sheets of "cut-film," such as is used for photographic negatives.[2] A more elaborate equipment may be advantageous, but it is not necessary for good work.[3] The author's present work-bench is shown in the frontispiece; it illustrates a number of points mentioned in the descriptions of the apparatus.[1]

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[1] Cf. Adams and Williamson, Jour. Franklin Inst., **195**, p. 485, 1923.

[2] It is best to remove the emulsion by soaking in hot water.

[3] It may be of interest to state the lack of equipment in the author's laboratory at Locust, New Jersey, from 1896 to 1912. There was no running water or modern vacuum system. There was no gas, a Berzelius alcohol lamp being used for the Bunsen burner, so that a mixture of sodium and potassium carbonates was used for the main fusion because the flame was not hot enough to melt sodium carbonate effectively. A "Primus" or "Khotal" burner served for high temperatures or for

1. Apparatus [2]

Balance and Weights [3]

Balance.—A reliable and accurate balance and a set of weights are essential for good analytical work. It cannot be too strongly impressed on the beginner that the value of his analytical work rests fundamentally on the quality of his balance and weights and on the care with which they are treated. The other apparatus may be adequate, the reagents of the utmost purity, the methods of the best, and the manipulation careful, delicate, and conscientious; but if the balance and weights are not accurate, and are not carefully taken care of, the labor and time expended on the analysis will largely go for naught. The balance and weights should, therefore, be regarded with a feeling akin to reverence, and the balance-case looked upon, so to speak, as a *sanctum sanctorum.*

There are many good balances, of moderate cost, now on the market that will answer the requirements for any but the most exacting work. Only a high-grade, analytical (not the so-called "student's") balance, of a reliable make, should be selected. In the present book the balance is assumed to be of the usual type. The author has had no experience with such new forms as those that utilize torsion instead of swinging the beam vertically, use a chain instead of weights, or place the

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a blast. Evaporations (with or without a water-bath) were conducted on small kerosene stoves. There was no hood with a proper draft. Distilled water was prepared in a Jewell's distilling apparatus (heated over a kerosene stove) or was bought specially prepared (and tested by the author for impurities) in ten-gallon carboys. Analyses of several rocks made under these primitive conditions were repeated in his present laboratory with very satisfactory and concordant results. He does not, however, advocate the use of such primitive laboratory equipment.

[1] The author is indebted to Mr. J. Harper Snapp, of the Geophysical Laboratory, for this photograph.

[2] In connection with many of the pieces of apparatus references are made to the catalogues of the Central Scientific Company, Chicago, edition of 1927 (C. S. Co.); Eimer and Amend, New York, edition of 1927 (E. & A.); the Fisher Scientific Company, Pittsburgh, edition of 1928 (F. S. Co.); and of Arthur H. Thomas, Philadelphia, edition of 1921 (A. T. Co.), so that the correct form may be identified. These will be referred to by the above abbreviations.

[3] Blasdale, pp. 8–23; Fresenius–Cohn, 1, pp. 12–25; Gooch, pp. 11–24; Hillebrand–Lundell, pp. 7–14; Mellor, pp. 3–27; Treadwell–Hall, pp. 3–7; P. J. Krayer, The Use and Care of a Balance, 42 pp., Easton, Pennsylvania, 1913. The author is indebted to Mr. Krayer for reading this section and making valuable suggestions.

smaller weights (as riders) on an attachment to the beam instead of by hand on the pan. These types will, therefore, not be considered here.

The capacity of the balance should be 200 grams, with a sensitivity of one-tenth of a milligram at full load. The bearings (both knife-edges and planes) should be of agate, the beam of some light and not easily corrodible metal and graduated for a rider.

As summarized by Mellor, the conditions that must be satisfied by a good balance are: (a), it must be *consistent*, that is, give the same result in successive weighings of the same body; (b), it must be *accurate;* (c), it must be *stable*, so that the beam after being displaced will return to its horizontal position; (d), it must be *sensitive;* (e), in order to avoid loss of time in weighing, the beam must oscillate quickly, and should therefore be short.[1]

It will be convenient to adjust the sliding scale or screw on the pointer so that one small division of the scale corresponds to 0.1 milligram. The zero-point should be ideally at zero on the scale. But the author agrees with Wells [2] that far too much importance has been laid on the zero-point being at the exact center of the scale. It should be not more than one or two small divisions away, on either side, as will be mentioned in the section on "Weighing" (p. 94). The position of the zero-point, whether central or not, should be ascertained frequently and especially before beginning an analysis, but not before each weighing, as is recommended by some. Balances vary much as to the persistence in preserving the zero-point unchanged.

In readjusting the zero-point by moving the nuts at the ends of the beam, it should be remembered that this end of the beam *expands through the heat of the hand*, so that the beam must be allowed to cool off for a long time (at least one-half hour) after each adjustment and the zero-point taken again. The student must pay especial attention to this precaution. The zero-point should be readjusted *as seldom as possible*,—an argument against the zero-point being fixed at the exact center of the scale.

The balance must, of course, be in a case, with appropriate releases for the knives and pans. The case is always to be *kept closed* when the balance is not in use, a precaution often disregarded, and always to the detriment of the balance.

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[1] This (*e*) is of less importance than the other points; all the first four are essential to good work.

[2] H. L. Wells, Jour. Am. Chem. Soc., **42**, p. 411, 1920. Mr. Krayer (an authority on balances) is fully in agreement on the non-importance of the zero-point, so long as it is near the center of the scale.

There is no need of keeping a desiccating agent in the balance-case, and this very common practice *should not be followed.* No drying agent is effective, because the air within changes every time that the case is opened, and its presence may be positively harmful. If a desiccant is used, it should be granular soda-lime, which is placed in a 2-inch funnel supported in a small Erlenmeyer flask, and placed at the back of the case near the middle. One of the new perchlorate desiccants may serve, but they may give off dangerous acid vapors. *Sulphuric acid must never be used as a desiccant in a balance-case.* It is liable to form SO_2 by the action of dust, and there is always danger of overturning the beaker or of the acid overrunning by absorption of water. Calcium chloride, also, is objectionable because, as was pointed out by Mr. Krayer, the glass panes inside the case tend to become bedewed with moisture. In general, *there should be no desiccant* of any sort *within the balance-case.*

The case, balance, and pans are to be kept free from dust by an occasional light brushing with a soft and long camel's hair brush, not with a cloth. The balance or pans must never be washed, especially with alcohol.

A balance reading-glass (C. S. Co., 820; E. & A. 17142) placed in front of the pointer is very useful in reading the pointer and increases the accuracy of the weighings. Another very useful adjunct is a rubber hand-bulb, connected with a tube passing through the floor of the case and permitting a *puff* of air to be blown against the bottom of one of the pans, preferably the left-hand one.[1] The beam is thus started swinging gently, without any danger of touching the pan by the ordinary method of waving the hand. There should be provided a small, light metal stand for holding tubes (E. & A. 17132; F. S. Co. 2-210; A. T. Co. 9974), as well as a small shelf to straddle the pan for specific gravity determinations.

The location of the balance is a matter of importance. The essential points are:

1. The balance should be in a room separate from the laboratory, where it will be free from corroding gases.

2. It should be located so that the two arms will maintain, as nearly as possible, the same temperature, and consequently the same length. Hence it should not be placed near a window, especially one with southern exposure, or a source of heat, such as a radiator, stove,

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[1] So far as the author knows this is provided only with the Rueprecht balances. It should be better known and more widely used, as it is, by far, the best device for the purpose.

or hot-air vent. It must not be placed where it will be in direct (or even reflected) sunlight at any time of the day or year.

3. The source of light, especially if artificial, should be above and back of the head of the observer, and so located with respect to the beam that the heat from it will affect both arms equally. Diffuse daylight from a window at one side, if somewhat in the rear of the observer and not very near, will answer.

4. The foundation upon which the balance-case stands should be firm and solid, and not subject to any jarring or vibration from machinery. A heavy stone slab with stout legs (which may be made of iron piping) answers well.[1] The top must be strictly horizontal and there should be sufficient space on it for the notebook and desiccator.

The balance should be in such a position that the rod which serves to move the riders does not project beyond the table or so that it may be touched in passing by the table.

Certain precautions are to be observed in the use of a balance.[2] Among them the following are important: the balance-beam is to be kept *raised off the knife-edges when the balance is not in use;* the beam should always be lowered or raised *slowly and carefully;* the beam must *never be free to swing* while the weights or other objects are being placed on or removed from the pans, or when the rider is shifted; care should be taken not to overload the balance. See also the section on weighing (p. 94).

Weights.—The weights should be of the "first quality" of the catalogues. The set should run from 100 grams to 1 centigram. The weights below the ten milligram weight are not needed, as the rider is always used instead. The gram weights are best made of brass, preferably gold- or platinum-plated, though Krayer advocates the use of first-quality lacquered brass weights. The smaller weights are of platinum. The weights may be kept in their box (covered) in front of the case, though some prefer to keep them, arranged in order, in the balance-case in front of the right-hand pan.

The weights must never be touched with the fingers, but are always to be handled with the ivory-tipped forceps that should accompany them. The handling with these should be most gentle, and there must be no rubbing or scraping of the neck of the larger weights in putting them back in their places. They must be kept free from the action of any dust or corroding vapors, and must never come in contact with any solid or liquid chemicals. If kept in the box, this is always to be closed after use. The weights are to be occasionally lightly wiped (not rubbed) with a silk handkerchief. Still more, they must never be washed with alcohol or any other liquid.

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[1] The brass or glass balance-rests of the legs may be placed on rubber stoppers to reduce vibration, if there is machinery in motion near by.

[2] Blasdale, p. 7; Hillebrand–Lundell, pp. 12–14; Mellor, p. 7; Treadwell–Hall, pp. 5–7.

For accurate work the weights should be calibrated. The description of this process is rather long, and the student is referred to the following authorities.[1]

One must be certain that the rider is of the weight appropriate to the divisions on the beam, as it has happened that a 12-mg. rider has been used on a beam that is divided into tenths, or the converse.

It is assumed that the laboratory has a cheaper or less accurate balance, capable of weighing up to one kilogram or so, and a set of weights, to weigh out reagents roughly and in large amounts.

Platinum

A number of utensils of platinum are indispensable for the chemical analysis of rocks. The present price of platinum is so high that, for some chemists, who are not the fortunate possessors of an old stock, a substitute for platinum must be used when possible.

Platinum is used as the pure metal and as alloys with small percentages of iridium or of rhodium. The behavior and relative merits of these have been studied by many workers, especially by the Bureau of Standards at Washington, D. C.[2]

From these investigations it appears that pure platinum is not only too soft and pliable for general use, but that it also loses weight by volatilization. Iridium (up to about 2 per cent) stiffens it, but this metal is more volatile than platinum; so that the loss of weight on ignition may become serious. The addition of a small amount (about 4 per cent) of rhodium to pure platinum stiffens the metal, as does iridium. The loss on ignition of iridium-platinum is greater than with pure platinum and much greater than with rhodium-platinum. Rhodium-platinum would seem to be the best platinum alloy for general use. The author has had no experience with it, and can not say how it compares with palau for the sodium carbonate fusion.

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[1] Blasdale, p. 18; Mellor, p. 16; Treadwell–Hall, p. 16; Hillebrand–Lundell, p. 12.

[2] For some studies on the quality and properties of various platinum wares on heating see: R. W. Hall, Jour. Am. Chem. Soc., **22**, p. 494, 1900; Hulett and Berger, Jour. Am. Chem. Soc., **26**, p. 1512, 1904; Hillebrand, Walker, and Allen, Jour. Ind. Eng. Chem., **3**, p. 686, 1911; Burgess and Sale, Jour. Ind. Eng. Chem., **6**, p. 452, 1914; **7**, p. 561, 1916; Bull. Bur. Standards **12**, p. 289, 1915 (Sci. Paper 254); Burgess and Waltenburg, Bull. Bur. Standards **13**, p. 365, 1916 (Sci. Paper 280); Hillebrand, Bull. **700**, p. 102 (note 3), 1919; Hillebrand–Lundell, pp. 18–20.

There are several alloys that serve as substitutes for platinum.[1] The chief of these is ''palau,'' an alloy of 80 per cent gold and 20 per cent palladium, which has been in use for some years. From long experience the author has found it to be far superior to iridium-platinum, and still more to pure platinum, *for the sodium carbonate fusion,*[2] because the cold cake loosens readily from the crucible and does not stick as it is apt to do with the other two. For other purposes it is almost as satisfactory, except that it is somewhat more readily attacked by the pyrosulphate fusion than is platinum or iridium-platinum. The alloy is also acted on by hot, strong hydrochloric acid, as in the evaporation for silica (p. 157), the palladium dissolving slightly and leaving the gold exposed. This, however, has not been observed to affect the analysis seriously.

''Rhotanium'' is the trade-name of another alloy of palladium and gold similar to palau, and ''auranium'' and ''platino'' are the trade-names for alloys of gold and platinum, all of which have been suggested as substitutes for platinum in the form of crucibles, etc. The author has had no experience with these.

The use of fused silica (''vitreosil'') instead of platinum is discussed on page 178.

All or nearly all platinum and palau crucibles lose weight[3] (palau less than platinum), when heated above about 900° C, especially on blasting (about 1200° C). With platinum the loss is mainly due to the iridium content. The rate of loss for each crucible used should be ascertained; or, if serious, the empty and cleaned (not scrubbed with sand) crucible should be weighed after an ignition.

✓ **Care of Platinum.**—There are several precautions to be observed in the use and care of platinum[4] and palau utensils.

Platinum utensils must be kept bright and clean; this applies especially to crucibles. It is best accomplished by rubbing the crucible with sea sand moistened with water—the author has found sand from the New Jersey coast to be excellent. The whole lot of sand should be well washed, digested with warm, dilute, hydrochloric acid for some time, to remove fragments of shells, and then washed again and dried. The crucible should be sand-rubbed occasionally, as this prevents and removes surface crystallization and coating, and greatly prolongs the life of the crucible. Firmly adherent particles of ignited precipitate or stains[1] may be removed by fusing a little potassium pyrosulphate in the crucible. If the stain is on the exterior, the salt is fused in a larger crucible or in a small basin in which the crucible to be treated is immersed. Because platinum is somewhat attacked by molten pyrosulphate this fusion should not be continued longer than is necessary.

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[1] F. A. Fahrenwald, Jour. Ind. Eng. Chem., **9**, pp. 590–597, 1917; Gurevich and Wichers, Jour. Ind. Eng. Chem., **11**, pp. 570–573, 1919; Hillebrand, Bull. **700**, p. 44; Hillebrand–Lundell, pp. 18–20.

[2] H. S. Washington, Jour. Washington Acad. Sci., **11**, p. 9, 1921.

[3] Cf. Hillebrand, Bull. **422**, p. 94, footnote; Burgess and Sale, Jour. Ind. Eng. Chem., **6**, p. 452, 1914; **7**, p. 561, 1916; Sci. Paper Bur. Standards, **254**, 1915; Burgess and Waltenburg, Sci. Paper Bur. Standards, **280**, 1916.

[4] Cf. Mellor, p. 115; Hillebrand–Lundell, p. 19.

Red-hot platinum or palau must never come in contact with any other metal. Therefore, during an ignition a platinum crucible must be supported in a platinum triangle or in one of iron or nichrome with the wire covered by fused silica tubing or pipe-stem, while only the latter should be used for a palau crucible. The red-hot crucible should be handled only with the platinum-tipped tongs, although tongs tipped with chromel may be used if the platinum or palau is *not red-hot.* In heating the platinum basin over a Bunsen burner it is well to have the center of the gauze asbestos-covered. No metals or salts of heavy or easily reducible metals should be heated or melted in platinum or any of its alloy substitutes.

Sulphides, arsenides, and phosphides must never be heated in platinum. Therefore, the ignition of phosphates, as that of magnesium, must be carried out very cautiously to avoid the presence of a reducing atmosphere inside the crucible, such as is caused by too high a flame. This often results in a ruined, perforated crucible.

Fused sodium and potassium carbonates[2] attack platinum very slightly, but fused caustic alkalies attack it very seriously. Platinum is appreciably, but not seriously, attacked by fused potassium pyrosulphate, so that the crucible shows a slight loss of weight after each fusion with this salt (p. 188).

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[1] A brownish stain sometimes develops after ignition, due to the oxidation of iron present in the platinum. This may be removed by fused pyrosulphate, and it is well to boil a new platinum crucible in hydrochloric acid. Iron is now seldom met with, at least to a serious extent. Cf. Hillebrand, Bull. **700,** p. 44; Hillebrand–Lundell, p. 18; L. Duparc, Bull. Soc. Franç. Min., **42,** p. 156, 1919. Duparc thinks that the stain is caused by the transfusion of the gas through the hot metal and its reducing action on the iron silicates of the rock.

[2] Melted lithium carbonate strongly attacks platinum, so that it cannot be used for the alkali carbonate fusion, as has been suggested.

As the metal is readily attacked by chlorine, platinum must never be exposed to this gas, whether in solution or free. Consequently, it should never come in contact with a mixture of hydrochloric acid and an oxidizing agent which would give rise to free chlorine. If manganates are present, they should be reduced, as by alcohol, before the addition of hydrochloric acid.

Platinum should not be exposed to burning carbon, as coke or coal, though the *flameless* burning off of the carbonized filter paper does no damage. Platinum must not be heated in a smoky or luminous flame. Therefore, the air supply of the Bunsen burner must be adjusted so that the flame is non-luminous. Also, the crucible must never come in contact with the inner cone of the Bunsen burner. The use of the Meker burner obviates this possibility.

Platinum should not be exposed to violent changes of temperature, such as exposure when red-hot to a blast of cold air or immersion in water, and the crucibles must not be bent nor squeezed, all of which are frequently recommended, to loosen a fused cake. A little care and patience will obviate the need of such measures, and the loss of a little time is preferable to the misfortune of dented and distorted, and possibly cracked and ruined, crucible.

List of Apparatus.—One platinum basin, lipped, of about 300 c.c. capacity, 10 to 11 cm. across the top, and about 5 cm. deep, weight about 100 grams. This should not be hemispherical, but with a somewhat flatly rounded bottom and vertical upper sides, (E. & A. 29880; A. T. Co. 8311). If the edge is stiffened with wire this should not be continued around the lip, or, if so, the turned-down edge should be soldered with platinum around this, to prevent entrance of liquid and possible contamination or loss. Instead of a platinum basin one of palau or of chemically pure gold (free from copper) will serve, and good porcelain may be used in work that is not very accurate, although it is difficult to remove all silica from this. Neither fused silica nor glass should be used for the main evaporation to determine silica.

Four crucibles; two of 30 to 35 c.c. capacity,[1] and two of about

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[1] One crucible should be of palau, for the sodium carbonate fusion. Hillebrand–Lundell (p. 28) suggest that if only two platinum crucibles can be purchased they should be of 25-c.c. capacity. I would prefer one of 30 c.c. and one of 20 c.c. The former size serves best for the sodium carbonate and pyrosulphate fusions, and the ignition of the ammonia precipitate, which is often too bulky for a small crucible; while a 20-c.c. crucible will answer for most ignitions. A palau crucible is not necessary, but is desirable.

20 c.c. Each should have its own cover, with which it is always to be weighed. A palau crucible serves best for the main fusion with sodium carbonate, because the cake is freed from this metal much more easily than from crucibles made of platinum or iridium-platinum,[1] and it is possibly better in this respect than rhodium-platinum.

One Gooch crucible, 3½ cm. wide at the top, and 2¼-2½ at the bottom, of about 25 c.c. capacity, which should have a cover. A close-fitting cap for the bottom of this crucible is a convenience. A porcelain or fused silica Gooch may be used instead.

One small, lipped, flat-bottomed basin, of about 50 c.c. capacity, and weighing about 20 grams.

One spatula, in one piece, about 15 cm. long and weighing about 15 grams. It should be rather thick, with a round, broad end. A second spatula, about 10 cm. long and weighing 8 to 10 grams, will also be useful.

Two triangles, one of 5 and one of 6 cm., along the side. The style with twisted ends is good, or if the ends are smooth it is well to make a series of small notches along one end to support a crucible cover and prevent its slipping when the crucible is placed on its side in the triangle (p. 120).

As some platinum crucibles may adhere to platinum triangles, triangles of clay or fused silica have advantages other than those of low cost, and are indeed recommended. Those made of silica tubing or pipe-stems strung on nickel or nichrome wire answer well in place of platinum. If one has both platinum and palau crucibles and triangles, the different metals must never be in contact when hot.

One perforated, seamless cone, about 2.5 cm. in diameter.

One pair of crucible tongs, of brass or German silver, tipped with platinum, and of the usual shape. One of Blair's form, with platinum shoes, will also be useful[2] but is not indispensable.

A pair of blowpipe forceps, with platinum tips, (C. S. Co. 1486; E. & A. 23606; F. S. Co. 10-290) is necessary for blowpiping, and is very useful in separating mineral grains for analysis.

A few small pieces of platinum foil, cut into strips and bent at right angles or in zigzags, are used to prevent boiling liquids from "bumping" (p. 213).

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[1] H. S. Washington, Jour. Washington Acad. Sci., **11**, p. 9, 1921.

[2] Cf. Hillebrand, Bull. **700**, p. 33; Hillebrand-Lundell, p. 21; Mellor, p. 113. Such tongs do not appear to be listed in any of the dealers' catalogues. They are sold by Baker & Company, Newark, N. J. These tongs are shown in the frontispiece at the extreme right. They are not necessary, however, as brass tongs of the usual bowed shape may be used (p. 215).

A foot of platinum wire (about No. 27) is used for blowpiping, and pieces will serve to prevent bumping.

GLASS[1]

There are now produced in the United States several makes of chemical glassware, some of which are equal to, and in some respects excel, the best of German glassware.[2] Of these "Pyrex," a borosilicate glass,[3] is especially valuable because of its very low coefficient of expansion, which permits thicker walls and consequently less danger of breakage. It is also therefore very slightly affected by sudden changes of temperature. Pyrex is highly resistant to the action of various solutions of acid, alkalies, and salts, as well as hot water. Similar resistant chemical wares such as "Insol," Nonsol," and "Vineland" makes, are lime-soda glasses.

Beakers.[4]—These should be on hand in liberal quantity. They should all be lipped and of the usual (Griffin) form; the tall forms and beakers without a lip are seldom if ever needed. It is convenient to have a small space ground or etched on the side, so that the beaker may be marked with a pencil. The following number of each size should be kept at hand: Three 1000-c.c., four 800-c.c., six 500-c.c., ten 250-c.c., ten 200-c.c., ten 150-c.c., five 50-c.c.

Beakers should be of Pyrex glass, or at any rate some of resistant glass, such as Jena.

Burettes.—It is best to have two types of these. There should be two Ripper's[5] weight-burettes (C. S. Co. 1952; F. S. 3-825), one of 50 and one of 100 c.c. for the iron oxide determinations. These should have glass caps to cover the tips, and a wire loop to support them above the balance-pan.

Some advantages of a weight-burette over the usual form are:[6]

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[1] See Hillebrand–Lundell, p. 16, for remarks on chemical glassware, with a table of analyses of typical varieties. See also articles by G. W. Morey and by W. E. S. Turner in Intern. Critical Tables, **2**, pp. 87 and 107, 1927.

[2] Cf. Walker and Smither, Jour. Ind. Eng. Chem., **9**, p. 1090, 1917.

[3] Jena glass is a borosilicate glass containing zinc.

[4] Cf. W. D. Collins, Jour. Ind. Eng. Chem., **13**, p. 1072, 1921. Several beakers of the form and proportions used by me are shown in the Frontispiece.

[5] M. Ripper, Chem. Zeit., p. 793, 1892. Cf. Kolthoff–Furman, Vol. Anal., pp. 10–12.

[6] R. S. McBride, Bull. Bur. Standards, **8**, p. 617, 1912; see also E. W. Washburn, Jour. Am. Chem. Soc., **30**, p. 40, 1908; Hillebrand–Lundell, p. 127; Kolthoff–Furman, Vol. Anal., p. 10.

Correction for temperature changes is not needed, adherence of liquid to the walls is of no consequence, the solutions can be weighed readily to 0.01 gram, whereas measurement to 0.01 c.c. is very uncertain.

If the burette becomes stained brown by manganese, the stain may be removed with a little dilute hydrochloric acid. After the burette has been used it should be very thoroughly washed.

There should also be two burettes of the ordinary Mohr's type (C. S. Co. 1918; E. & A. 19166; F. S. Co. 3-7050; A. T. Co. 2414), with Fresenius stopcock, preferably set at an angle of 90°. These are of 50 c.c., graduated to tenths of a cubic centimeter, and should be "certified." Such devices as Erdman's float, meniscus reader, and Schellbach enameled strip on the back are not needed.

Color Comparison Tubes.—A simple form of these will serve for the determination of titanium and manganese if one of the more elaborate colorimeters is not available. These should be of the tall form, marked at 50 c.c., better also at 100 c.c. It is not necessary that they be glass-stoppered. A stand with inclined mirror below is sold by the dealers. A more accurate form is the Eggertz tube, either the straight or the Julian type with bent end to facilitate mixing. No stand is needed for these. For their use see page 197.

Crystallizing Dish.—A crystallizing dish, with straight walls, will serve as a trough for holding the ice-water for cooling the flask after reduction by H_2S in the ferrous oxide determination (p. 140). Its width may be about 8 inches and its depth 4. One with thick walls is not liable to be broken. An enamelled iron basin, rather deep and of suitable dimensions, will serve admirably.

Desiccators.—One desiccator, 6 inches in diameter, either of the Scheibler form (C. S. Co. 3770; E. & A. 21850; F. S. Co. 8-595; A. T. Co. 4436), or that of the Atwater (A. T. Co. 4444), serves for general use. A perforated porcelain plate is used with the Scheibler form, and a pipe-stem triangle for that of the Atwater. Granulated soda-lime, anhydrous calcium chloride, or "dehydrite" should be used as the drying agent. *Sulphuric acid should not be used,* because it may give off sulphur dioxide by the action of dust and because of its liquid form. It is convenient to have also a larger Scheibler desiccator, containing a porcelain plate with several holes, in which crucibles, etc., can be put aside. A Scheibler desiccator with a stopcock for drying *in vacuo* is sometimes useful, but is not necessary for general work. A little vaseline, lightly rubbed on the edges of the body and of the cover, may be used.

Drying Cylinders.—A good type of drying cylinder, or the so-called calcium chloride jar, is that with the perforated glass stopper and side-tube near the top (C. S. Co. 2303; E. & A. 22556; F. S. Co. 2-910; A. T. Co. 2718). Two or three of medium sizes will serve.

Drying Tubes.—These are best of the U shape, and preferably of the Schwartz type. Three or four, of medium sizes will do.

Filter Crucible.—A filter crucible of Jena glass (E. & A. 23030) with integral porous bottom of fritted glass may be used in place of the platinum Gooch with asbestos (p. 116).[1]

Filter Flask.—One of the Erlenmeyer form, with side tube, and with stout walls (C. S. Co. 5664; E. & A. 23070; F. S. Co. 10-175; A. T. Co. 5430), is needed for filtration under suction (p. 113). A convenient size is 500 c.c. It is not necessary that it be of Pyrex glass, but this is best.

Filter Tube.—(C. S. Co. 6124; E. & A. 23130; F. S. Co. 8-260; A. T. Co. 5314). One should be selected of a size to fit the Gooch crucible that is in use, with allowance for the rubber connection. The tube is to be provided with a singly-perforated rubber stopper to fit the filtering-flask.

Flasks.—Both the ordinary flat-bottomed and the Erlenmeyer shapes may be of the following sizes: Ordinary flat-bottom; two each of 400, 200, 100, and 50 c.c.; Erlenmeyer flasks, three each of 500, 300, and 200 c.c. These should be of Pyrex glass.

Funnels.—To be properly efficient a funnel must have perfectly *straight and conical* sides, which should have an apical angle of exactly 60°. If the sides are not straight the paper cannot be made to fit, although departure from an apical angle of 60° may be corrected by proper folding of the paper filter. The rim should be ground.

The stems of funnels as usually sold are too short and wide for rapid filtration. For many years the author has used the so-called Piccard's tube[2] attached to all funnels for regular filtrations, as do all the chemists in the Geophysical Laboratory. We find them to be very advantageous and suitable for quantitative work, contrary to the opinion of Mellor. They are to be made as follows:

The pointed end of a properly selected funnel is cut off square and there is fused to the cut-off stem a tube from 22 to 25 cm. long, with an internal bore of 3 mm., which near its upper end is bent into a vertical circle[1] of 2 to 2½ cm. diameter. It is important that the junction should be smooth, continuous, and without enlargement, and the tube narrow. The tube should also be *kept clean,* as by the use of a bichromate-sulphuric acid cleaning fluid from time to time. If these details are attended to there is no difficulty in filling the tube and maintaining a continuous flow. The gentle suction caused by the weight of the column of liquid greatly increases the speed of filtration.[2]

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[1] A Jena glass filter crucible is apt to crack around the junction of the porous plate and the sides if heated above 150° C. They can not be used for ignitions.

[2] Cf. Ostwald, p. 14; Mellor, p. 90; Blasdale, p. 148. This was invented by J. Piccard in 1865 (see Mellor). It is remarkable that such funnels, which have been in use for many years, are not listed in the dealers' catalogues.

The Piccard tube should be fused on to the stem, and *not attached by rubber tubing,* as was originally proposed and as is figured by Mellor and by Blasdale. The rubber tubing connection may lead to loss or contamination of the filtrate by creeping of the liquid between the rubber and the glass.

There should be two of the Piccard funnels of 75 mm., three 65 mm., and two 55 mm. in diameter, so that several filtrations may be made simultaneously.

A small funnel 3.5 to 4 cm. in diameter and with a straight and obliquely cut-off stem is needed for small filtrations, especially in the determination of the alkalies. Another funnel, 5 or 6 cm. in diameter, with the stem cut off half-way, slightly drawn out and bent through an angle of about 60°, is used for introducing acids into covered vessels, as hydrochloric acid into the platinum basin for the determination of silica. It is well to have at hand several other ordinary funnels, of different sizes.

Gas Generators.—Kipp's form (C. S. Co. 6896; E. & A. 24412; F. S. Co. 11-190; A. T. Co. 6000) is generally used and is one of the best. Schroder's automatic gas generator (F. S. Co. 11-195) has been found to be simpler and more efficient than Kipp's form. There should be one of each, of medium size, for carbon dioxide and hydrogen sulphide.

Gas-Washing Bottles.—A good type is Allihn's (E. & A. 18850; F. S. Co. 3-025; A. T. Co. 5989), and another about equally good is Drexel's tall form (C. S. Co. 7094; E. & A. 18844; F. S. Co. 3-035; A. T. Co. 5990). There should be two or three of medium sizes.

Glass Cells.—A pair of glass cells, with parallel sides and with identical internal distance between parallel sides may be used for colorimetric work, if one of the more complex clorimeters (p. 51) is not available.

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[1] The circle acts as a catch to start the filling of the tube below; without it the liquid might run down the walls without filling the tube.

[2] Two of these funnels, with the Piccard tubes fused on, are shown in the frontispiece toward the left.

Measuring Cylinders.—These should be lipped and not stoppered. They should be reasonably accurate, but it is not necessary that they be "certified." There should be one each of 10, 25, 100, and 500 c.c.

Measuring Flasks.—These should all be stoppered and should conform to the tolerances of error permitted by the Bureau of Standards.[1] One each of 1000 and 500 c.c., and three each of 250, 200, and 100 c.c. will suffice.

Pipettes.—Two each of 5 and 10 c.c. and one of 50 c.c., with the bulb in the middle of the stem, are sufficient. Their capacity should be indicated by marks above and below the bulb. Their tolerances should be those stated by Hillebrand–Lundell, p. 124.

Separatory Funnel.—One pear-shaped, separatory funnel, (C. S. Co. 6172; E. & A. 23684; F. S. Co. 10-435; A. T. 5630), with glass stopcock and stopper, and rather wide stem, may be needed occasionally for mineral separations with heavy solutions. A capacity of 125 c.c. is about the right size.

Specimen Tubes.—There should be a supply of several dozens of these, with round bottoms, and with smooth corks to fit. Appropriate sizes are: 4 x ½ and 5 x ⅝ inches, of which the first will be the most generally used.

Stirring Rods.—The diameter of these should be not over 3 mm.; beginners generally use stirring-rods that are too thick. About twenty should be prepared, of various lengths, and from 10 to 22 cm. long; the shorter stirrers being made of the thinner rod. Both ends should be rounded, and about 2 cm. of one end should be bent back sharply at about 60°. Stirring-rods that are *alike at both ends should not be used,* because of the danger of mistaking the immersed part (with adherent solution or precipitate) for the clean end.

One of the long and one of the medium stirrers should be provided with a rubber "policeman." The narrow shape (E. & A. 30734; A. T. Co. 8796) is the best for general use. One is readily made by covering the end of the rod with a short length of black gum tubing, with the end projecting about ½ cm., which is pressed down flat and *closed* by squeezing while warm with the tongs. This form is far superior to the so-called "wing" forms, and that made as a bag is very inefficient.

Test Tubes.—A few each of different sizes, from small to medium (say 10 x ½ to 16 x 2 cm.) should be kept at hand.

Thermometer.—A thermometer, which may have a white glass scale, reading to 150° C., is needed for the hot-air oven. It will also be well to have one or two others, with scale etched on the stem, reading to 300° C., for various purposes.

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[1] Cf. Hillebrand–Lundell, p. 123.

Tubing.—There should be on hand sufficient tubing of rather soft glass and of various diameters for making connections, etc. There should also be a supply of special glass tubing, of an internal diameter of 5 or 6 mm., for the determination of water. This tubing may be either thick-walled and of soft glass, or (better) thin-walled and of refractory glass, but not as refractory as combustion tubing (p. 243). The glass must not devitrify on heating, as sometimes happens with old glass. Several lengths of soft glass and Pyrex glass tubing adapted to making the Piccard's suction tubes for funnels (p. 41) should be on hand.

Wash-Bottles.—Two main wash-bottles are needed. These should be of Pyrex glass, flat-bottomed, and of 1000-c.c. capacity. The tip, with an exit hole 1 mm. in diameter, is attached by a short length of rubber tubing. About 5 c.c. of the lower end of the exit tube should be bent through an angle of about 60°, so that the intake is near the lower side-wall, and in the same side as the tip. This enables more of the liquid to be expelled than if the tube is straight.

The neck of one of these wash-bottles, used for hot water, should be covered, so as to protect the hand against the heat. This covering may be a thin sheet of cork, bent entirely around the neck and held in place by copper wire.[1] Cork is preferable to asbestos paper, which is liable to flake off and contaminate the material in the process of analysis. Wash-bottles with wicker-covered necks are now sold by the dealers, and are very satisfactory.

There should also be a wash-bottle (500 c.c.) reserved for the dilute ammonia water used in washing the magnesia precipitate, and another (300 c.c.) reserved for the alcohol used in the alkali determination. It is best to have these with glass stoppers (C. S. Co. 1770; E. & A. 18966; F. S. Co. 3-405; A. T. Co. 9830) because ammonia water and alcohol attack rubber, and it is well to label each specially.[2] A spare 300-c.c. wash-bottle will be convenient for various washing solutions.

Watch-Glasses.—Six of each of 2, 2½, 3, 3½, 4½, and 5 inches and three each of 6, 6½, and 7 inches should be on hand. It will be convenient to have one each of the 4-, 5-, and 6-inch glasses perforated with a central hole about 5 mm. in diameter. A watch-glass must always be placed on a beaker with the *convex side down.*

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[1] One is shown in the frontispiece.

[2] The wash-bottles with ground-in glass stopper, as usually sold by the dealers, are of very unsatisfactory shape, the neck being too long, and the tubes for the mouth and for the tip being at an awkward angle, and both of them too long.

A pair of 3-inch glasses of about the same weight should be adjusted to equal weight by filing down the edge of the heavier. These should be marked with a diamond pencil with initials, letter, and date. Watch-glasses of equal weight with handles are much preferable (E. & A. 17114; F. S. Co. 2-200). Such pairs of watch-glasses are to be used for weighing out fluxes, and are to be kept in the balance-case.

Fused Silica

Because of its high melting point,[1] resistance to all acids, (except hydrofluoric, and at high temperatures phosphoric), constancy in weight under ignition, and low coefficient of expansion, fused silica will replace the much more expensive platinum for many purposes,[2] such as most ignitions and the fusion with pyrosulphate. It can now be obtained of very good quality [3] and in a great variety of forms. Of the two varieties the transparent is the better, but is more expensive than the translucent, which will replace it for almost all purposes. The surface of the crucible or basin must be smooth and free from bubble cavities, which is the case with the best grades of the translucent variety. Strongly alkaline liquids should not be heated for long in fused silica vessels, although it is claimed that ammonia has no action on vitreosil. Fused caustic alkalies or the alkali carbonates attack fused silira, as do some metallic oxides at high temperatures.

Basin.—This must be lipped. One about 13 cm. in diameter and 7 cm. deep, with a capacity of about 500 c.c., will serve for the alkali determination, in default of one of platinum, palau, or gold.

Beaker.—It is well, but not necessary, to have a fused silica beaker for the alkali determination. This is best of 400-c.c. capacity, and must be lipped.[4]

Crucible.—A 30-c.c. "vitreosil" crucible ("high form"), with cover, may be used for almost all ignitions and also for the pyrosulphate fusion, if the small amount of silica is disregarded (p. 178).

It requires much more time to heat fused silica crucibles to the proper temperature and to cool them in the desiccator than those of platinum. Also, for ignitions a much higher temperature is needed. We have found, for instance, that it is sometimes impossible to ignite the lime, in ordinary amounts, to constant weight, as CaO, in a fused silica crucible over a large Meker burner, and that this could only be done by using a blast. Hillebrand-Lundell (p. 19) state that fused silica crucibles are easily electrified[1] and are slightly hygroscopic.

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[1] The fusing point or interval of vitreosil is between 1700° and 1800°. It can be used safely up to 1100°, or even 1350° for short periods.

[2] Hillebrand–Lundell, p. 29.

[3] "Vitreosil" is the trade-name of one of the best.

[4] One is seen in the frontispiece at the extreme left.

Gooch Crucibles.—A fused silica crucible may replace one of platinum or porcelain, asbestos being used with them. "Vitreosil" Gooch crucibles are made with a filtering layer of fritted fused silica powder, similar to those of Jena glass. They do not crack on heating, as do those of glass.

Triangles.—Fused silica may be used for triangles, instead of platinum or palau, as they are much cheaper and there is no liability of the crucible sticking to the triangle. Those made of fused silica tubing broken in pieces and strung on nickel or nichrome wire are better than those made in one piece, because the latter inevitably form grooves around the platinum crucible. For this reason the tubing should be broken into two or three short lengths on each side. This has, however, the disadvantage that, as the silica is brittle, the ends form dust or small grains on rubbing together; therefore, the usual pipe-stem triangle, which is far cheaper, is much to be preferred. One of the solid silica triangles, and a platinum crucible grooved by it, are shown in the frontispiece on the right.

PORCELAIN

Royal Berlin remains probably the best make of porcelain for chemical use, but the Coors, an American make, is also excellent. Recently the English and the Japanese have been making very good porcelain crucibles and other vessels. A new material, "Sillimanite," made of the mineral sillimanite instead of kaolin, is very highly spoken of, and would seem to be superior to porcelain in many respects. Furthermore, it is said to be less fragile.

Casseroles.—One or two casseroles of 165 and 135 mm., and possibly a smaller one, with porcelain handles, will be useful. Covers are not needed for these.

Crucibles.—Two or three of different small sizes, with covers, are useful. One about 5 cm. in diameter may be reserved as a "radiator"

[1] Dr. R. C. Wells suggests keeping a small piece of pitchblende in the balance-case to prevent this. (Personal communication.)

for the evaporation of sulphuric acid in platinum crucibles, but a nickel crucible is better for this (p. 49). A porcelain Gooch crucible, 35 or 40 mm. in diameter, may replace one of platinum, but a vitreosil or a Jena glass filter crucible is superior.

Evaporating Dishes.—Two or three each of 9, 10, and 15 cm., lipped, should be on hand.

Mortar.—A porcelain mortar, rough inside and glazed outside, with a porcelain pestle, is useful for powdering salts. It may be 10 cm. in diameter.

Plate.—A square, white, porcelain plate, 12 or 15 cm. in diameter, is useful for titrations, as well as for the separation of minerals.

Rings.—A set of porcelain rings should be provided for each water-bath. *Copper rings should never be used.*

RUBBER

Funnel.—A hard rubber funnel, of the smallest size, is needed for filtration of liquids containing hydrofluoric acid, if one of platinum is not available.

Stoppers.—There should be a selection of several sizes, perforated with one and two holes.

Tubing.—A variety of different sizes, for making connections, should be available. There should also be about one foot of black, soft, thin-walled gum tubing for Gooch crucibles (C. S. Co. 11618; E. & A. 30716; F. S. Co. 14-180; A. T. Co. 8846), of a diameter appropriate to the crucible in use and to the size of the filter tube.

It is assumed that the burners are provided with heavy-walled rubber tubing, preferably white (C. S. Co. 11582; E. & A. 30682; F. S. Co. 14-165; A. T. Co. 8830).

METAL

Burner (Blast).—A Bunsen blast-burner of the usual type is useful for glass-blowing, but the author has not found it to be often necessary for the analysis of rocks. A Meker burner can be substituted for it in almost all cases.

Burners (Bunsen).—At least four Bunsen burners should be available. The Tirrill type, (C. S. Co. 2133; E. & A. 19266; F. S. Co. 3-960; A. T. Co. 2582), which permits easy adjustment of both gas and air, is excellent.

Burners (Meker).—For higher temperatures than the Bunsen, the Meker type is best, an improved form being the Fisher patent, but those of this type that the author has seen are too large. A Meker burner is much superior in many respects to a Bunsen, and should be used instead of a blast.[1] It is a common error to use a Meker burner of too large a size, which gives much too large a flame. One of the smallest sizes, No. 1 or No. 2 of the catalogues, is best adapted for most purposes. The life of a platinum crucible heated over a Meker burner is much longer than that of one heated over a Bunsen burner, and still more so than over a blast.

Clamps.—There should be on hand several clamps of different sizes and kinds. A large-sized one of the "Universal" type (C. S. Co. 2898; E. & A. 30266; F. S. Co. 5-750; A. T. Co. 3202), with rubber-covered jaws, is used to hold the weight-burette. There should also be several clamp holders.

Hot-Plate.—An electric hot-plate with three degrees of heat is very useful. It may replace a steam-bath. *A sand-bath must never be used;* they are invariably rusty and the rust and sand are very apt to contaminate the material being analyzed.

Mortar.—A large steel, so-called Plattner diamond mortar is the best type for the preliminary crushing. The steel should be as hard as possible, to avoid contamination by iron. Many of the diamond mortars sold by dealers are unsatisfactory in this respect, and it is suggested that more attention be paid to this important feature by the manufacturers of steel mortars. Possibly a lining of "stellite" or "carboloy" on the bottom of the cavity and the face of the pestle might serve.

The type best known to the author, which the Geophysical Laboratory and the U. S. Geological Survey have used for many years, is that devised and made by Mr. C. W. H. Ellis, formerly mechanician of the Geophysical Laboratory. It is made of specially hardened "Ketos" steel. One of the large size, used in the Geological Survey laboratory, is figured by Hillebrand,[2] with its dimensions given.

These mortars are of the Plattner style, in three pieces, base, cylinder, and pestle, but the cylinder is very high, to guard against loss of fragments and dust. They are all larger than the Plattner "diamond" mortars ordinarily obtainable. The pestle may be of two forms; one with a large knob at the upper end (as figured by Hillebrand), for use with the hand alone, the pestle acting as hammer; and the other slightly tapering upward, and flat at the top, for use with a hammer. The base may be square or round. The bottom of the cavity in the base is *flat*,[1] the cylinder fitting snugly into the cavity, while the pestle has a little play in the cylinder. The dimensions of the one the author uses are: Base, 6 cm. square, 2.5 cm. thick; cavity, 3.2 cm. diameter, 0.5 cm. deep; cylinder, 8 cm. high, 3.2 cm. (scant) external and 2.6 internal diameter; pestle, 1.5 cm. long, 2.5 cm. diameter at base, 2.4 at top. The hardness of the steel is 8.

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[1] It may be of interest to state the temperatures of burner flames. In that of a Bunsen, the maximum temperature, 1560° C., is just above the inner dark cone, from here to the tip it is 1540° C.; in a Meker the whole of the upper flame is uniformly 1600° C., one half a centimeter above the grid it is 1720° C., while at the small blue flames it is 1770° C. (A. Stäbler, Handb. Arbeitsmethoden, **1**, p. 307, 1913.) Blasdale (p. 34) states the temperature of 805° C. is attained in an *uncovered* platinum crucible of 29 c.c. over a Meker burner, and one of 780° C. over a Bunsen. Much higher temperatures are attained if the crucible is covered. Cf. Hillebrand-Lundell, p. **99**.

[2] Hillebrand, Bull. **700**, p. 58. Hillebrand–Lundell, p. 670.

If one of these is not procurable, a first-quality, three-piece Plattner's "diamond" mortar may be used. It is important that the steel should be as hard as possible, a point to which especial attention should be paid, that the pestle should fit somewhat loosely in the cylinder, and that the bottom of the cavity and the end of the pestle should be flat. Those usually listed in the dealers' catalogues are intended for blowpiping, and are too small for convenient use with rock specimens, though they will serve.[2]

The steel mortar should be exposed as little as possible to the fume-laden atmosphere of the laboratory, and must be kept in a tightly closed tin box or can, to prevent rusting. It should not be handled with moist fingers, and after use it should always be wiped dry with a clean and dry cloth and placed in its box. The steel mortar must never be greased or oiled, however slightly.

Nickel Crucible.[3]—A nickel crucible, used as a radiator, is better than one of porcelain for the evaporation of sulphuric acid (p. 162), as the operation is more quickly carried out. One 5 cm. in diameter, 4 cm. high and of about 60-c.c. capacity, is of convenient size.

The author has not used the radiator figured by Hillebrand[4] because he finds the simple nickel crucible to be efficient, and nickel is far preferable to iron.

Oven.—A copper oven with single walls is needed. A convenient size is 8 x 6 x 6 inches. One shelf above the bottom is sufficient. The oven should be provided with legs or a suitable tripod support.

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[1] A hemispherical cavity, recommended in the first edition of this book (1904). was supplanted by a flat bottom in the second (1910) and third (1914) editions, Hillebrand, unfortunately, overlooked these corrections.

[2] A steel mortar is figured by Thornton (Titanium, p. 159). This is sold by Eimer & Amend (28686).

[3] Cf. W. M. Thornton, Jr., Jour. Ind. Eng. Chem., **3**, p. 419, 1911.

[4] Hillebrand, Bull. **700**, p. 33; Hillebrand–Lundell, p. 21.

Ring Supports.—At least three, and preferably four, should be on hand. The base should be rectangular, not triangular, as these are unstable. The rod may be 16 or 18 inches high, and about ¼ inch thick. Rings, with clamp attached, 3 and 4 inches in diameter are most useful. It is well also to have a 5-inch ring. One of the 3-inch rings should have three interior knobs for supporting the nickel crucible when evaporating sulphuric acid. It is unwise to have more than one ring on the stand at a time. The rod may be advantageously covered with a 6-inch section of glass tubing closed at the top, to prevent the falling of rust. The ring supports and rings should be wiped off frequently. There is constant danger of contamination by iron rust from them, and it is highly desirable that ring supports with the rods, if not the rings, made of stainless steel, nichrome, or some such non-rusting metal should be provided by the dealers.

Tongs.—The usual crucible tongs, "double bent," are used for general purposes. *They must not be of steel.* Brass or nickel-silver are best, preferably the latter. Those tipped with chromel may be used for handling hot platinum, instead of the more expensive platinum tips. But one pair of untipped brass tongs must be at hand for use in the determination of water, as hot glass adheres to chromel and platinum (see p. 245). Blair's tongs, about 7 inches long, made of chromel, of the form of platinum tongs figured by Hillebrand, would be very useful and would mostly replace those made of the more expensive metal.

Tripods.—Two tripod supports should be at hand, one to support the oven, and the other for heating the platinum basin in the manganese and phosphorus determinations, although a ring-support will serve. Tripod supports are not recommended for general use, because of their fixed height.

Water-Baths.—If the laboratory is not provided with a steam-bath, two water-baths should be at hand. These are to be of copper, and best fitted with a Kekulé regulator. The water- or steam-bath should be provided with porcelain rings; copper rings must never be used.

Wire Gauze.—Two squares each, of 4 and 5 inches, are needed. They are best made of nichrome wire, as these do not rust and long outlive those of iron. It is well to have also one with an asbestos-covered center for heating the platinum basin.

MISCELLANEOUS

Agate Mortar.—An agate mortar, about 9 cm. outside diameter, is needed for the preparation of the rock specimen. One should be selected that has no soft spots or crystalline streaks on the grinding surface. The pestle should be embedded in a wooden handle with cement,[1] and a brass collar, making the whole about 2½ inches long. It will be useful, but is not necessary, to have another larger agate mortar, about 13 cm. in diameter. The pestle of this needs no handle. *Substances should only be ground, never pounded,* in an agate mortar.

Burette Stand.—One for two burettes is needed. A very convenient type is the Chaddock (C. S. Co. 13073; E. & A. 31914; F. S. Co. 14-695; A. T. Co. 2516), with rubber-covered wire spring-clamps and white glass base.

Colorimeter.[2]—A colorimeter is needed for the colorimetric determination of titanium, manganese, and chromium.

There are several excellent forms of the "balancing method" types, in which the "test" and "standard" solutions are compared by being viewed through a plunger which varies the height of the column of solution seen through; when the two colors match or "balance" the concentration of the two solutions are *inversely* proportional to their heights. Of this type are the Kober, Campbell–Hurley, Duboscq, Schreiner, Steiger, and others. They are all more or less expensive and complex, but are very accurate if properly used. The author's experience has been only with the Kober instrument, the use of which is described on page 162, but any one of them should serve equally well for the titanium, manganese, or chromium determinations, and the general procedure would be, *mutatis mutandis,* that described here.[3]

A simple form, and one that is easy to make, is the Weller colorimeter,[4] modified and described by Hillebrand,[5] which has been used by the chemists of the U. S. Geological Survey for many years. This depends on the "dilution method," in which each solution contains the same weight of the substance per cubic centimeter.

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[1] The author's pestle-handle has been in use for over thirty-five years, and is still firm.

[2] See Yoe, Colorimetry, pp. 10–51, for descriptions of various types and their use; pp. 52–55 for the calculation of results; pp. 83–90 for errors. Cf. also Hillebrand–Lundell, pp. 24–26.

[3] The bottoms of the cups or cells should be fused on to the side-walls.

[4] A. Weller, Berichte, **15**, p. 2599, 1882.

[5] Hillebrand, Bull. **176**, p. 170, 1900; Bull. **700**, pp. 35–37; Hillebrand–Lundell, pp. 24–25; Mellor, p. 84. An improved, but less simple form is described by Steiger, Jour. Am. Chem. Soc., **30**, p. 215, 1908; Hillebrand, Bull. **700**, p. 37. It is now used by the chemists of the U. S. Geological Survey laboratory; the author has never used it.

Because of the high cost of the more complex forms, the making of this is described here.

The essential part of the simple form is a pair of glasses or glass cells, of square or rectangular section. Two opposite sides of each must be parallel, and the interior distances apart of these sides in the two glasses must be identical, at most within one per cent of the distance. The other sides need not, but would best be parallel, and may be blackened to exclude light. The glasses used by the author are 12 cm. high, and 4 cm. between the parallel sides each way.

These glasses are made of thin (2-3 mm.) plate glass, cut to size and cemented with a cement that will resist the action of dilute acids. The angles may be strengthened by rubber tape.

The use of a suitable box is necessary to exclude side lights, and that illustrated by Hillebrand serves well. This may be easily made from a box in which are packed the ceresine bottles containing one-half pound of ammonia water or hydrofluoric acid.

The box measures 20 x 9.5 x 9.5 cm. internally. The square bottom is removed, leaving the box open at both ends. A 3-inch square of ground glass is substituted for the sliding cover, the glass slipping snugly into the grooves, which may need a little widening with a penknife. About 5 cm. of the side next to the free edge of the glass is then cut away, to allow the insertion of the pair of glasses. This side now becomes the top of the box. A thin wooden partition (made of the box cover) is inserted through a narrow slot cut clear across the top of the box alongside the glasses away from the ground glass. This shutter should slide stiffly up and down, so as to remain at any desired height, or a thin wedge may be used to hold it in place. The box and partition are blackened inside and out, and the result is a box that is light and compact enough to be held easily in the hand.

Cork Mats.—Three or four cork mats on which to place glass vessels are useful. These are made of thin sheet cork about four inches square.[1]

Filter Papers.—Round-cut filter papers are to be used, the paper being of such quality as to leave a negligible amount of ash, filter fairly rapidly, and yet retain the precipitate. They must be "double washed" with hydrochloric and hydrofluoric acids.[2]

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[1] Two of these are shown in the frontispiece.

[2] Hillebrand–Lundell, p. 89.

The Schleicher and Schüll papers are among the best. Nos. 589 and 590 are the most frequently used qualities. No. 589 (black ribbon) is soft and loose, and filters rapidly; it is most appropriate for the alumina and similar precipitates. No. 589 (white ribbon) is more retentive and is the most generally useful. No. 590 filters more slowly but retains the finest precipitates. The ash of No. 589 is negligible, unless three filters of large size are used (as in the case of alumina). The Whatman papers are also excellent; Whatman No. 41 corresponds to Schleicher and Schüll 589 (black), No. 40 to S. and S. 589 (white), and 44 to S. and S. 590.

The sizes in regular use are: 5½-, 7-, 9-, 11-, and 12½-cm. The filters are to be kept in a drawer away from dust.

Funnel Supports.—Three wooden funnel supports should be sufficient. The author's preference is for the single-arm type for two funnels, with one hole larger than the other. The two-arm types take up unnecessary space, and the arms cannot be differently adjusted as to height.

The long supports for six to ten funnels, so much in favor with industrial chemists, have no place in the chemical analysis of rocks. In an industrial laboratory, where many identical filtrations are made simultaneously, the fixity of height is advantageous; whereas, in rock analysis, where simultaneous filtrations are of very different substances, this is very disadvantageous. Such supports, also, occupy much space.

Labels.—A box of medium small gummed labels, such as Dennison's No. 217, should be on hand.

Sieve.—A sieve[1] for preparing the rock powder is made of a cylindrical glass crystallizing dish, about 8 cm. in diameter and 4½ cm. high, preferably with thick walls. Closely fitting this is a brass band[2] about 1 cm. wide which holds in place a 4-inch square of silk bolting-cloth. To prevent the loss of dust (p. 83), the brass band may be 2 cm. wide and a second crystallizing dish of the same diameter as the first, fitting into the upper half of the ring, acts as a receptacle for the rock powder.

Silk Bolting Cloth.—The type that is best for preparing the sample is of 100-mesh (40 meshes to the centimeter). Three square feet of this had best be kept. Some of 50-mesh will be useful for mixing the sample (p. 85).

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[1] Sieves such as these are useful for many separations, and they might well be listed in the dealers' catalogues.

[2] An adjustable band may be made of an old steel clock-spring, cut to an appropriate length.

Spoon.—One of horn, about 12 cm. long, is used for weighing out fluxes. It may be conveniently kept in the balance-case.

Stone Slab.—A useful adjunct is a small slab of some igneous rock, such as granite, on which to cool crucibles. This may be 4 x 3 x 1 inches, and is polished on the top face. A steel block of about the same size may be used, but this should be nickel- or gold-plated to prevent rusting. The small granite slab used by the author is shown in the frontispiece, on the extreme right.

Reagents

The quality of reagents[1] is most important, and is a matter that is far too often neglected. Only reagents of the *very best quality* should be used, and *these should not be taken on faith.* One must test even the so-called ''guaranteed'' or ''analyzed'' reagents for impurities, by the methods suggested by various authors,[2] and in some cases for impurities not considered by them. This is necessary because, although they are generally satisfactory, yet mistakes occur and it is very difficult to free some reagents from certain impurities. As Hildebrand says: ''A C.P. label is no guarantee of the purity of a reagent,'' and samples of ''guaranteed'' reagents have occasionally been found to be worse than some without any special guarantee.[3]

Sodium carbonate and potassium bisulphate, which are all-important for the analysis of rocks, are difficult to procure of thoroughly satisfactory quality, and the same is true of the calcium carbonate that is used for the determination of the alkalies. Microcosmic salt and alkali phosphates in general are apt to contain insoluble matter derived from the glass container. Their solutions should be filtered before use. Ammonium carbonate may contain sodium salts, but in recent years this has become one of our purest reagents. Ammonia water is often of very unsatisfactory quality, being sold and kept in ordinary glass bottles.[1] The "guaranteed" grades of mineral acids (including hydrofluoric) in this country are of excellent quality and their purity can, in general, be accepted, except for special purposes. Hydrogen peroxide nowadays seldom contains fluorine.

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[1] Fresenius–Cohn, **1**, p. 49; Hillebrand, Bull. **700**, pp. 45–47; Hillebrand–Lundell, pp. 31–34; Mellor, p. 141; Treadwell–Hall, p. 45.

[2] Fresenius–Cohn, Qual. Anal., p. 106; Quant. Anal., **1**, p. 127; C. Krauch, The Testing of Chemical Reagents for Purity, New York, 1902; E. Merck, Chemical Reagents, their Purity and Tests, New York, 1929; B. L. Murray, Standards and Tests for Chemical Reagents, New York, 1929; E. White, Analytical Reagents, London, 1918.

[3] In the Geophysical Laboratory "guaranteed" ammonia has been found to contain zinc; potassium chromate crystals of potassium nitrate; ammonium acetate much cadmium; and magnesia about 3 per cent of lime. Cf. Hillebrand–Lundell, p. 31.

Concentrated acids, ammonia water, and hydrogen peroxide are intended throughout this book, unless it is stated that they are dilute. In this case the proportion of acid (by volume) is placed first.

In recent years there has been a great improvement, and the "guaranteed reagents" made in this country are generally excellent.

It is well to stock up with amounts of reagents (except the strong acids and ammonia), sufficient to last for some time, and to test each new lot once for all.

All the reagents in use are to be kept in glass-stoppered bottles[2] of good quality; the narrow-mouth ones (best with vertical flat stoppers) are to be *kept covered with loose-fitting caps,* and the wide-mouth ones should have a flat stopper projecting over the lip to keep off dust. It is best, when possible, to have the label either etched or ground on the glass or, better, enameled. Paper labels should be varnished. The strength of standard solutions should be written on the label.

As stated by Hillebrand–Lundell (p. 38), it is not well to make up stock solutions of most of the solid reagents, because of their solvent action on glass.[3] This applies especially to ammonium oxalate and sodium ammonium phosphate. Such solutions should be prepared as needed.

It may be convenient to give a list of the different sizes of reagent bottles appropriate for the reagents in most general use. Most of these are and all ought to be obtainable of the dealers, in these sizes with permanent labels as mentioned above.

Narrow-mouth Bottles, 500 c.c.—Alcohol, ammonia,[4] ammonium molybdate, ammonium nitrate, hydrochloric acid, nitric acid, standard potassium chromate solution, standard manganese solution, magnesia mixture, silver nitrate, standard titanium solution, sulphuric acid (concentrated), sulphuric acid (1:1).

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[1] The ammonia sold in ceresine bottles often reaches the consumer in containers that are empty or only partly filled, because of cracks or leakage. It should *always be filtered before use* to free it from particles of ceresine.

[2] Cf. Mellor, p. 142.

[3] Magnesia mixture (prepared as on page 61), chloroplatinic acid, ammonium molybdate, and boric acid, used for the determination of FeO, are exceptions, as are the "standard solutions."

[4] This bottle should be coated internally with ceresine or paraffin, or a ceresine bottle should be used in place of glass.

250 c.c.—Acetic acid, barium chloride, chloroplatinic acid, ether, hydrogen peroxide, potassium thiocyanate.

Wide-mouth Bottles, 500 c.c.—Ammonium chloride, ammonium oxalate, calcium carbonate, ferrous sulphide, sodium ammonium phosphate, sodium carbonate, potassium pyrosulphate.

250 c.c.—Ammonium nitrate, asbestos, sodium acetate, potassium nitrate.

In the following list of reagents (with the exception of alcohol, ammonia, hydrochloric, hydrofluoric, nitric, and sulphuric acids), amounts are suggested that should be sufficient to last several years, in ordinary analytical work. They should all be "guaranteed," with the exception of the few that are noted, and all should be tested as to purity.

Acetic Acid (250 grams).—Acid of 30 per cent strength will answer for most purposes.

Acid, Hydrochloric (6 pounds).

Acid, Hydrofluoric (two 8-ounce bottles).—This must be obtained and kept in ceresine bottles (never in rubber, gutta-percha, or bakelite). The *greatest possible caution* should be observed in the use of hydrofluoric acid, as a burn produced by it may last for years.

Acid, Nitric (7 pounds).

Acid, Sulphuric (9 pounds).

Alcohol, Ethyl, Absolute (8 ounces).—This is only used in the determination of strontium. The stopper should be very close-fitting Absolute alcohol readily absorbs water from the atmosphere.

Alcohol, Ethyl, "95 per cent" (2 quarts).—This should be of good quality, not denatured, and it *should be filtered.* For use in the determination of the alkalies it is diluted with distilled water to a specific gravity of 0.86. If a hydrometer is not available, this specific gravity may be attained approximately by mixing five volumes of alcohol with one of water. The liquids are to be measured out separately because of the contraction that takes place on mixing.

Ammonia (4 pounds).—This name will be used throughout instead of ammonia water or ammonium hydroxide, following the usage of Hillebrand, Mellor, and Treadwell–Hall. This reagent must leave no solid residue on evaporation, and it must be free from carbonate, but it is seldom necessary to test it with barium chloride for CO_2. If ammonium carbonate is present the ammonia should be boiled for a few minutes.

Ammonia "guaranteed" may be purchased in ceresine bottles, but its delivery in this material is not a guaranty that it has not been kept in glass.[1] It is best to make it by passing ammonia gas from a cylinder through (previously boiled and cooled) distilled water contained in a ceresine bottle. This should be *only half full,* to allow for expansion, and *surrounded with water and cracked ice.* The gas should be passed until the specific gravity is 0.92. The purity of the reagent thus prepared will compensate for the trouble involved.

Ammonia intended for analytical work must never be kept in unprotected glass, as this is inevitably attacked more or less, rendering the reagent impure.[2] Pyrex glass is less readily attacked than is ordinary glass, but even it should not be used for the storage of ammonia.

Allen and Johnston [3] studied the action of ammonia on glass, and obtained very considerable residues from ammonia kept in bottles of ordinary glass, less in Pyrex, and none in ceresine.

Ammonia is best kept in ceresine bottles, with tight-fitting ceresine stoppers that are closed by a screw motion, and covered with a loose-fitting cap or a small beaker. It may be kept in a glass bottle that has been coated thickly over the interior with ceresine, by putting a few pieces into the perfectly dry bottle, gently warming it, and spreading the wax by turning the bottle around. This coating, however, even if it is very thick, is likely to loosen in time and allow the ammonia to attack the glass, so that a ceresine bottle is preferable.

Ammonium Carbonate (1 pound).—This should contain no non-volatile matter and only a trace of tarry matter. The solution is made as needed.

Ammonium Chloride (1 pound).—This is not likely to contain impurities that render it unfit for the alkali determination, for which alone it is used, but it should be tested to see that it does not contain non-volatile matter or alkali chlorides. Resublimation is seldom called for. It should not be used for the addition of ammonium chloride in the main portion of the analysis, where it is formed by the neutralization of hydrochloric acid by ammonia.

Ammonium Molybdate (1 pound).—This salt is usually sufficiently pure for use without testing. The solution used in the determination of phosphorus pentoxide is prepared by dissolving 30 grams of ammonium molybdate in 500 c.c. of water by the aid of heat, with constant stirring. The mixture is filtered through an asbestos plug in a funnel, after standing for a few days.

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[1] Ammonia from ceresine bottles must be filtered, to rid it of particles of ceresine. One should use a large quick-filtering paper, the funnel to be kept covered with a watch-glass during the filtration.

[2] Small siliceous flakes may be seen floating in almost any ammonia that is kept, even for a short time, in ordinary glass.

[3] Allen and Johnston, Jour. Ind. Eng. Chem., **2**, p. 202, 1910.

The author has not for some years used the solution of ammonium molybdate in nitric acid, formerly recommended.[1] It is awkward to prepare and does not keep well.

Ammonium Nitrate (8 ounces).—A solution containing 340 grams of this to the liter is used in the determination of phosphorus pentoxide, and the salt is occasionally used in the solid form.

Ammonium Oxalate (1 pound).—It is well to recrystallize this, after filtering to insure freedom from calcium oxalate. The salt may be dissolved as needed, or may be kept as a saturated solution (filtered) in a 500-c.c. bottle. One hundred cubic centimeters of this contains 0.5 gram of ammonium oxalate.

Ammonium Persulphate (2 ounces).—The ordinary pure salt will answer for the colorimetric determination of manganese, but for the precipitation of manganese with alumina the ''guaranteed'' salt should be specially tested, or purified by the method recommended by Hillebrand.[2] The salt is used in the solid form. Potassium periodate is now always used in the Geophysical Laboratory instead of ammonium persulphate (p. 250).

Asbestos[3] **(4 ounces).**—This must be of the anhydrous amphibole variety, insoluble in acids, and perfectly white and silky. It must not be of the chrysotile or serpentine variety, which is partially soluble in acids and contains about 13 per cent of water, which is lost on ignition, resulting in the breaking down of the fibrous texture.

A good quality, perfectly white, silky, but not necessarily very long fiber, should be selected. About 10 grams is macerated with water in a porcelain mortar, or if of long fiber is scraped down with a knife and macerated with water. The mass is placed in a 400-c.c. beaker, 200 c.c. of water and 20 c.c. of hydrochloric acid are added; the mixture is boiled for half an hour, and allowed to stand over night. It is then well washed with distilled water, and preferably allowed to stand again over night with dilute acid to remove all soluble iron.

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[1] Washington, Manual, 3d ed., p. 48. Cf. Hillebrand–Lundell, p. 38.

[2] Hillebrand, Bull. **700**, p. 112. Hillebrand–Lundell (p. 35) recommend that the purest obtainable salt be purchased and corrected for impurities by a blank determination.

[3] Hillebrand–Lundell, p. 91. Cf. Dana, System of Mineralogy, 1892, pp. 389, 670.

Finally, it is thoroughly washed with hot water on a large filter (best with suction) to free it from chlorides, and kept, mixed with enough water to make a thin cream, in a wide-mouth, glass-stoppered bottle. There should be no coarse bits of fiber in the final product.

Ascarite.—See Soda-asbestos.

Barium Chloride (4 ounces).—A solution of 20 grams in 200 c.c. of water is used.

Boric Acid (4 ounces).—This is to be used in the titration for ferrous oxide (p. 212). Either the crystal of powder form will serve, of the "C.P." quality. It is kept in saturated solution.

Bromine (1 ounce). Saturated bromine water[1] may be needed for the precipitation of manganese (p. 170). It is fairly permanent in the dark, but it is best to make it up as needed.

Calcium Carbonate (1 pound).—This is in the powder form, not too fine and light. Only the very best quality of specially prepared calcium carbonate should be used, and the amount of alkali (reckoned as NaCl) in 8 grams properly sampled should be determined by the Smith method (p. 220), so as to be able to apply the proper correction.

This is done by rubbing up 8 grams (weighed to 1 centigram) of the calcium carbonate with 0.5 gram of ammonium chloride, and treating the mixture exactly as if the alkalies were being determined in a rock. The finally weighed chlorides may safely be assumed to be wholly NaCl, and the treatment with chloroplatinic acid dispensed with. Hillebrand (Bull. **700**, p. 208) and Hillebrand-Lundell (p. 788) state that "8 grams of carbonate will yield usually from 0.0012 to 0.0016 gram of alkali chlorides, almost entirely the sodium salt." The stock of carbonate used in the Geophysical Laboratory, specially prepared and washed contains a negligible weight of alkalies in 8 grams. This determination must never be neglected when dealing with a new lot. If the carbonate is of really good quality, containing less than half a milligram of NaCl in 8 grams, the correction need not be applied, except in very accurate work. If the alkali salts are present in more than this amount the whole lot of calcium carbonate is to be rejected, or more thoroughly washed with hot water.

Calcium Chloride (1 pound).—This should be the granular form of the anhydrous salt, for use in drying apparatus, and the ordinary "pure" quality will serve.

Chloroplatinic Acid (10 grams).[2]—As it is usually obtained this contains about 37 per cent of platinum. It is used as a solution containing either 0.05 or 0.10 gram of platinum per cubic centimeter. The author's preference is for the former. To make this, 10 grams are dissolved in 50 c.c. of cold water, filtered through a very small filter, the filter washed several times, and the filtrate made up to 75 c.c. in the reagent bottle. For the calculation of the proper amount to use in the analysis see page 232.

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[1] A saturated solution contains about 3.6 grams of bromine in 100 c.c. of water.

[2] Hillebrand–Lundell, p. 39.

Cupferron[1] **(50 grams)**.—This ammonium salt of nitrosophenyl hydroxylamine, $C_6H_5(NO)O.NH_4$, may be needed for the gravimetric determination of titanium (p. 200) and for others. The dry reagent should be kept in a cool, dark place, and the solution should be made up as needed.

Desiccating Agents.[2]—The student had best consult Hillebrand-Lundell, who discuss at length the choice of desiccants. Those usually employed are calcium chloride and sulphuric acid.

Several of the perchlorates have been recently introduced as dehydrating agents.[3] One of these is "dehydrite," magnesium perchlorate trihydrate; another is "dessichlora," anhydrous barium perchlorate; and pumice impregnated with anhydrous magnesium perchlorate has also been suggested. They are said to be very efficient, without liquefaction, and are easily rejuvenated. Any of these may be used in desiccators or in place of anhydrous calcium chloride in the determination of CO_2. The ability to rejuvenate them possibly offsets their rather high cost.

Dimethylglyoxime (1 ounce).—A little of this is dissolved in alcohol as needed for the determination of nickel.

Ether, Ethyl (8 ounces).—This should be anhydrous.

Hydrogen Peroxide (8 ounces).[4]—Any good brand that contains at least 3 per cent of H_2O_2, such as "dioxogen" or the stronger (30 per cent) "perhydrol," will serve. The latter is to be preferred, because it contains no acetanilide. It is scarcely necessary nowadays to test for fluorine, the only likely impurity that will affect its use for analysis, except acetanilide. If desired, this may be done by the method suggested by Hillebrand. As the reagent decomposes on standing, especially in warm weather or in a warm place, the bottle should be loosely stoppered, (perhydrol especially), and it is best to purchase it fresh, in small quantities, from time to time. Its strength may be tested by the method described in Hillebrand–Lundell (p. 35, note 24).

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[1] O. Baudisch, Chem. Ztg., **33**, p. 1298, 1909; **35**, p. 913, 1911; Baudisch and King, Jour. Ind. Eng. Chem., **3**, p. 629, 1911; W. M. Thornton, Jr., Am. Jour. Sci., **37**, p. 173, 1914; Thornton, Titanium, p. 90; Treadwell-Hall, p. 157; Hillebrand-Lundell, p. 109.

[2] Hillebrand-Lundell, pp. 43-46; Mellor, pp. 117-118.

[3] Cf. Smith, Brown, and Ross, Jour. Ind. Eng. Chem., **16**, p. 20, 1924; G. F. Smith, ditto, **19**, p. 411, 1927; Yoe, McGahey, and Smith, ditto, **20**, p. 656, 1929.

[4] Hillebrand, Bull. **700**, p. 46; Hillebrand-Lundell, p. 35; Mellor, p. 205.

8-Hydroxyquinoline (100 grams).[1]—This recently introduced reagent (also called "oxine") serves for several separations and determinations. It is especially useful in rock-analysis for the determination of magnesium (p. 208) and also for that of beryllium (p. 275). It is rather expensive and may be obtained from the Eastman Kodak Company, Rochester, N. Y.

A solution of the reagent is used. The solvent may be alcohol (5 per cent), as originally suggested by Berg. Acetic acid, however, is preferable, because it is "more stable and keeps for many weeks without change." As suggested by Kolthoff and Sandell [2] the solution may be made by dissolving a sufficient amount of the finely powdered reagent in $2/N$ acetic acid (say 36 c.c. of 30 per cent acetic acid and 64 of water) to form a 5 per cent solution; 10 c.c. of this is sufficient to precipitate 0.04 gram of MgO.

Iron Sulphide (2 pounds).—The ordinary fused, granular or stick form, is used for generating hydrogen sulphide.

Litmus Paper.—A little of both the blue and red will be useful. It may be obtained in a small book form or in strips in vials, and is best kept in a wide-mouth glass-stoppered bottle, painted black or kept in the dark.

Magnesia Mixture.[3]—The strongly ammoniacal magnesia mixture that is commonly recommended should not be used, because it attacks the glass bottles in which it is kept. For this reason Kuhnt [4] suggested the use of neutral solutions, which Hillebrand–Lundell improve on by adding hydrochloric acid. Magnesium chloride is better than the sulphate, because of the liability of the latter to give precipitates of basic magnesium sulphates (Mellor). Magnesia mixture may be prepared according to the directions of Hillebrand–Lundell, and is to be used instead of that recommended in the last edition of this book.

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[1] R. Berg. J. Prakt. Chem., **115**, p. 178, 1927; Zs. Anal. Chem., **71**, pp. 23, 369, 1927. Hahn and Vieweg, *ibid.*, **71**, p. 122, 1927. J. Robitschek, J. Am. Ceramic Soc., **11**, p. 587, 1928. Lundell and Knowles, Bur. Standards, Jour. Research, **3**, p. 91, 1929. Hillebrand–Lundell, p. 114.

[2] Kolthoff and Sandell, Jour. Am. Chem. Soc., **50**, p. 1901, 1928.

[3] Hillebrand–Lundell, p. 39; Mellor, p. 597.

[4] O. Kuhnt, Chem. Ztg., **44**, p. 586, 1920.

"Dissolve 50 grams of $MgCl_2.6H_2O$ and 100 grams of NH_4Cl in 500 c.c. of water. Add ammonium hydroxide in slight excess, let stand overnight, and filter if a precipitate appears. Make just acid with hydrochloric acid, dilute to one liter, and keep in a glass-stoppered bottle."

Marble (5 pounds).—Any good grade of white marble, not dolomitic, in lumps, will serve to generate carbon dioxide. As some marble contains sulphides, the gas must be washed with a solution of copper sulphate as well as with water.

Methyl Orange (1 gram).—The solution is made by dissolving 2 cgm. of the dye in 100 c.c. of water. It is most conveniently kept in a small dropping-bottle.

Methyl Red (1 gram).—This is best prepared by making up a 2 per cent solution in 60 per cent alcohol.

Microcosmic Salt.—See Sodium Ammonium Phosphate.

Paper, Macerated.—Macerated paper is used in the final precipitation with ammonia (p. 173), and some is best made up beforehand, as follows: Two or three 11-cm. ashless filters are torn in pieces, placed in a small beaker, and moistened with just enough concentrated hydrochloric acid to wet them. After standing for two minutes (not longer), distilled water is gradually added, the mass is vigorously stirred, whereupon the paper disintegrates rapidly. The product is freed from the acid by washing under suction and kept, mixed with enough water to make a cream, in a small, wide-mouth bottle. It should be properly labeled so as to distinguish it from asbestos.

Perchloric acid[1] **(4 ounces).**—This reagent is used instead of chloroplatinic acid for the separation of potash from soda. It may be purchased of good quality, but may be prepared by Kreider's method,[2] best as modified by Mathers,[3] or by that of Willard.[4] These are not described here, as descriptions of them are readily accessible, and as the use of the perchlorate method for potassium is not recommended in this book (p. 236).

Phenolphthalein.—A little of this, dissolved in alcohol, is occasionally used in testing for alkalinity.

Platinum Chloride.—See Chloroplatinic Acid, p. 59.

Potassium Fluotitanate (1 ounce).—This is preferable to titanium dioxide for the preparation of the standard titanium solution, as it is more readily obtainable pure, but potassium titanium oxalate, which contains no fluorine, and is readily obtainable, is much to be preferred. The fluotitanate should be recrystallized[1] and heated at 150° C. for two hours to render it anhydrous, and kept in well-stoppered bottles.

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[1] Hillebrand–Lundell, p. 37.

[2] D. A. Kreider, Zs. Anorg. Chem., **9**, p. 342, 1895.

[3] F. C. Mathers, Jour. Am. Chem. Soc., **32**, p. 66, 1910.

[4] H. H. Willard, Jour. Am. Chem. Soc., **34**, p. 1480, 1912.

Potassium Nitrate (1 ounce).—This is occasionally needed for oxidizing sulphides. It is used in the solid form.

Potassium Periodate (1 ounce).—This is used, instead of ammonium persulphate, for the colorimetric determination of manganese (p. 250). It is rather expensive, and is made by Erbach and Son Co., Ann Arbor, Michigan. It is sold by some dealers in chemicals.

Potassium Permanganate (1 ounce).—A solution of a concentration appropriate for use in rock analysis is made by dissolving 1 gram (best weighed to 1 milligram) of the pure, dry salt in 1 liter of water.[2] The solution should stand for one week to completely oxidize any organic matter in the water, and is filtered through previously ignited asbestos (placed as a loose plug in a rather large funnel)[3] into the stock-bottle, before standardization.

The stock-bottle for the permanganate solution is one of about 2 liters in which mineral acids or ammonia water are sold. The bottle should be painted black all over, and is best kept in the dark. One gram or 1 c.c. of this solution will be equivalent to approximately 0.0025 Fe_2O_3 or 0.00225 FeO.

The standardization may be affected with any of the well-known reagents,[4] such as ammonium ferrous sulphate, oxalic acid,[5] or ammonium, potassium, or sodium oxalate. The last is the one recommended.[6] Sodium oxalate ($Na_2C_2O_4$) is readily obtainable pure and dry.[7] It should be dried for two hours at 110° C. in the oven. The author's procedure, which is essentially that of McBride and Blum, except as to temperature, is as follows: One portion, of about 0.33 gram, of the sodium oxalate is weighed out to a tenth of a milligram, dissolved in water and placed in a 500-c.c. measuring flask, filled to the mark, and after shaking, 100 c.c. is measured out in a 100-c.c. flask. To this portion in a 400-c.c. beaker, 5 c.c. of 1 : 1 sulphuric acid is added and the volume is brought up to 250 c.c. It is then titrated (from a weight-burette) at room temperature[1] with the permanganate solution, the liquid in the beaker being vigorously and continuously stirred during the titration. The decolorization takes place *very slowly at first,* more slowly than with ferrous oxide, and one must wait until the liquid is decolorized before adding another portion of permanganate.[2] The permanganate is to be added in portions, at first, of not more than 1 c.c., and is "not to be added more rapidly than 10-15 c.c. per minute, and the last ½ to 1 c.c. must be added dropwise with particular care to allow each drop to be fully decolorized before the next is introduced." The end-point is reached when the *first pink blush* is obtained that does not disappear with a few minutes' vigorous stirring. For all but the most accurate work, the estimation of the "excess of permanganate used to cause an end-point color by matching the color in another beaker containing the same bulk of acid and water," is an unnecessary refinement. The depth of color decided on as the end-point may vary slightly with different individuals, but that used in the standardization must be adhered to in the iron determinations.

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[1] Hillebrand–Lundell, p. 458.

[2] For descriptions of the preparation and different methods of standardization of the solution, see Treadwell-Hall, pp. 96–99; Mellor, p. 193; Thornton, Titanium, p. 141; Kolthoff–Furman, Vol. Anal., **2**, pp. 282–296; Hillebrand–Lundell, pp. 144–147. Also see page 183 of the present book.

[3] It is best to use a perforated platinum cone, which will prevent any fibers from passing into the liquid.

[4] Iron wire should never be used. Cf. Hillebrand, Bull. **700,** p. 120, note 3; Hillebrand–Lundell, p. 147; Kolthoff–Furman, Vol. Anal., p. 290; Treadwell–Hall, p. 513.

[5] Treadwell–Hall (p. 512) objects to oxalic acid because of its water of crystallization. Hall and Smith (Jour. Am. Chem. Soc., **44,** p. 546, 1922), on the other hand, recommend it.

[6] Cf. Mellor, p. 193; R. S. McBride, Jour. Am. Chem. Soc., **34,** pp. 394, 415, 1912; Bull. Bur. Stand., **8,** p. 611, 1912; W. Blum, Bull. Bur. Stand., **8,** pp. 719, 726, 1912.

[7] A thoroughly reliable, certified, sodium oxalate is issued by the Bureau of

Three 100-c.c. portions of the sodium oxalate solution, prepared as described, are to be standardized as above.

The mean of the three determinations, which should not vary more than 0.01 gram, is taken, and will be, for the amounts above, about 30 grams of permanganate solution. As equal amounts of permanganate are required to oxidize one molecule of $Na_2C_2O_4$ (molecular weight = 134) and two molecules of FeO (molecular weight = 144),

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Standards, Washington, D. C., in bottles of 120 and 200 grams. It should be kept in the original bottle, closely stoppered, and best in a large desiccator. Sodium oxalate, specially purified for standardization, is now sold by dealers in chemicals.

[1] McBride and Blum titrate at from 60° to 80°. The author's preference is for room temperature, because this corresponds to that at which the ferrous oxide is determined, and because of the condensation of steam on the weight-burette over hot water and the possibility of not wiping it perfectly dry before weighing.

[2] For the mechanism and stages of the oxidation of oxalic acid by permanganate see Kolthoff-Furman, Vol. Anal. 2 p., 282.

1 cc weighs .001[illegible]

500 [illegible] g. in 1 c.c.
1.3

1.0746
.0006
.00064476 per c.c. FeO

the weight of oxalate per cubic centimeter is to be multiplied by 144/134 = 1.0746, to give the equivalent per cubic centimeter in terms of FeO.[1]

This divided by 0.9, or multiplied by 1.11, will give the value per cubic centimeter for Fe_2O_3. The solution of permanganate is stable[2] if kept out of contact with dust and reducing gases, and especially in the dark. According to Bruhns[3] the solution of really C. P. potassium permanganate keeps very well, whereas one of the ordinary salt does not. According to Blum the addition of 1 per cent of KOH increases the stability, but the author's practice is not to add this. In any case the standard solution *must be kept in the dark* and away from the fumes of the laboratory, the top covered with a glass cap or beaker. The sodium oxalate solution does not keep, and must be made up fresh for each standardization.

Potassium Pyrosulphate (1 pound).[4]—This must contain no silica, alumina, or iron. The pyrosulphate of either potassium or of sodium may be used; the author prefers the potassium salt. As the effective molten salt during the fusion of the alumina precipitate (p. 180), is pyrosulphate ($K_2S_2O_7$), this will be known as the pyrosulphate fusion.

The salt must be perfectly white and without any black specks. In its best form it is coarsely crystalline,[5] although it is usually fine-grained, hard, and porcelain-like. For such products, which are the result of too prolonged heating, and which contain some K_2SO_4, a few drops of concentrated sulphuric acid may be added to the coarse powder in the crucible before beginning the fusion. The salt should not froth or spatter on melting or during fusion.

If the pyrosulphate is not procurable of the proper quality, it may be made by fusing in the platinum basin the purest bisulphate, $KHSO_4$, at a low temperature until it ceases to spatter and copious white fumes of SO_3 come off. It is allowed to cool and is broken up, as described below. It is best, however, to make the reagent by melting together equivalent weights of the purest normal potassium sulphate (K_2SO_4)[1] and sulphuric acid in a platinum basin. Thus, one may take 87 grams of K_2SO_4 (in powder or small crystals) and 88 c.c. of concentrated sulphuric acid, which will furnish enough pyrosulphate for many analyses.

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[1] If ammonium oxalate is used, the factor is 1.596, and it is 1.6000 for oxalic acid. In either case the acid or the salt is to be recrystallized and dried in the desiccator. Because of the water of crystallization these two are not as reliable as sodium oxalate.

[2] Cf. Mellor, p. 196; Treadwell–Hall, p. 514. A standard solution of the author's that gave a value of 0.002497 gram Fe_2O_3 per gram on January 12, had one of 0.002480 on November 1, of the same year, that is, a loss of about 0.6 per cent.

[3] G. Bruhns, Chem. Ztg., **47,** p. 613, 1923; Chem. Abstr., **17,** p. 3145, 1923.

[4] Hillebrand, Bull. **700,** p. 46; Hillebrand–Lundell, pp. 34 and 704.

[5] One especially good lot, made from K_2SO_4 as described below, was found to be a mixture of 62 $K_2S_2O^7$ and 38 $KHSO_4$.

The fusion in the platinum basin supported on wire gauze is at first cautious and over a low flame, as the liquid is apt to bubble and spatter at first.[2] The flame is gradually raised, and the heating is continued until *dense* fumes of SO_3 are given off, and the liquid is clear and almost or quite free from the dark carbonaceous matter that is present at first. The molten mass should be tested from time to time by putting a drop, taken up with the small end of the platinum spatula, on a watch-glass, much as is done in the making of some candies. It is properly "cooked" when the cold drop is no longer waxy or crumbles, but is hard and free from liquid acid. The drop should be translucent. The mass in the basin is allowed to become cold,[3] and is then broken up into small pieces in a porcelain mortar with an agate or porcelain pestle, not on an iron slab. The dark portions near the edge are to be rejected.[4]

Hillebrand prefers the sodium to the potassium salt, because it melts more quickly and the cake is more easily soluble. The author's preference is for potassium pyrosulphate because the progress of the solution can be more readily watched during the fusion, and also the sodium salt has usually a greater tendency to spatter.

Potassium Sulphocyanate (1 ounce).—A solution made by dissolving 10 grams in 100 c.c. of water is used for detecting ferric iron. It is kept in a dropping-bottle.

Potassium Titanium Oxalate (1 ounce).—This is used for preparing the standard titanium solution (p. 68). It is preferable to potassium fluotitanate because it contains no fluorine.

Silver Nitrate (1 ounce).—A solution containing 3 grams to the liter is used in the colorimetric determination of manganese by the persulphate method. Of this 500 c.c. may be made up. About 100 c.c. of a stronger solution may be kept in a small dropping-bottle for testing filtrates for chlorine.

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[1] This should be tested for SiO_2, Al, and Fe.

[2] This fusion should be conducted under the hood.

[3] The large cake frees itself readily from the basin, aided by a little gentle pressure at the sides.

[4] Potassium pyrosulphate, as thus prepared, is used by all the chemists in the Geophysical Laboratory.

Soda-asbestos ("Ascarite").[1]—This absorbent for CO_2 is highly recommended by Hillebrand–Lundell; therefore it may be recommended here, although the author has not used it, to replace soda-lime. Its cost is high, but this is offset by its greater efficiency.

Soda-lime [2] (1 pound).—This should be porous and not hard. It is most effective for the absorption of CO_2 when it contains about 2 per cent of water. It would probably be better to use soda-asbestos ("Ascarite") in its stead.

Sodium Acetate (4 ounces).—This is to be kept in the solid form.

Sodium Ammonium Phosphate, (Microcosmic Salt) (8 ounces).—This is best kept in the solid form and the solution made as needed. It is convenient to keep a saturated solution in stock, but this is inadvisable because the glass is attacked by the liquid. The solution must always be filtered, even if freshly made, as the solid salt attacks glass and the liquid is apt to contain floating silica.

Sodium Carbonate [3] (2 pounds).—For many years anhydrous sodium carbonate has been used for the main fusion (p. 148). It was, however, very difficult to obtain the salt of a satisfactory degree of purity, as Hillebrand and others have pointed out. During the past few years the Geophysical Laboratory has been using the monohydrate, $Na_2CO_3.H_2O$, in its stead for this purpose, because the monohydrate is more readily obtainable free from impurities.[4] New stock should always be tested for the most serious impurities, silica, alumina, and iron oxide. According to Hillebrand–Lundell the total amount of impurities should be less than 2.5 mg. in 20 grams. In the following pages the monohydrate will be intended wherever sodium carbonate is mentioned, although the remarks will apply equally well to the anhydrous salt.

A mixture of equal parts of sodium and potassium carbonates melts at a lower temperature than sodium carbonate.[5] This mixture is sometimes recommended and was used by the author in his home laboratory (p. 29), but with proper gas burners its use has been abandoned, as the sodium carbonate is more effective at the higher temperature.

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[1] Hillebrand–Lundell, pp. 41–42. G. L. Kelley, Jour. Ind. Eng. Chem., **8**, p. 1038, 1916.

[2] Cf. Hillebrand–Lundell, p. 41.

[3] Hillebrand, Bull. **700**, pp. 46, 94; Hillebrand–Lundell, pp. 33, 700; Mellor, p. 163. For the testing of sodium carbonate see Hillebrand–Lundell, p. 33.

[4] An excellent quality is furnished by Mallinckrodt Chemical Works, St. Louis, Mo.

[5] M. P. = 690° C. Cf. Blasdale, p. 227; Mellor, p. 163; Hillebrand–Lundell, p. 701.

Sodium Oxalate[1] **(4 ounces).**—It is important that this salt, for the standardization of permanganate, should be perfectly pure and dry. A specially purified sodium oxalate is furnished by the Bureau of Standards, in Washington, D. C., and the dealers now sell the salt, of very great purity, for this purpose.

Standard Solution, Chromium.—This is prepared by dissolving 0.1276 gram of pure, normal potassium chromate (K_2CrO_4) in water and making up to 500 c.c. This contains 0.0001 gram of Cr_2O_3 per cubic centimeter. ok this wt.

Standard Solution, Manganese.—This should contain 1 mg. of MnO in 10 c.c. It is prepared by dissolving 0.1114 gram of the purest, dry, potassium permanganate in 250 c.c. of water. After standing for a day or two, 10 c.c. of sulphuric acid is added, and the permanganate is reduced by the very cautious addition of a solution of sulphur dioxide in water, until the solution *just* becomes colorless. When cool, it is to be diluted to 500 c.c. in a measuring-flask. ok

Standard Solution, Titanium.[2]—This should contain approximately 0.01 gram of TiO_2 in 10 c.c. It was formerly suggested that potassium fluotitanate ($K_2TiF_6.H_2O$) be used for the preparation of the standard solution of titanium. This salt may be obtained very pure. The complete expulsion of fluorine is tedious, but its removal is necessary because of its bleaching effect on the color of the peroxidized titanium solution. For this reason Merwin[3] prepared fluorine-free solution of titanium by heating titanium dioxide with ammonium persulphate and then dissolving the mass in sulphuric acid. He later tried potassium titanium oxalate[4] for the same purpose, and the author is indebted to him for the suggestion of its use, which has not been published by him. This salt is readily obtainable, being used in commerce for tanning leather, fixation of color in fabrics, etc., and the best grades are very pure. The composition of the salt is $K_2TiO(C_2O_4)_2.2H_2O$; it therefore contains 22.56 per cent of TiO_2. It must be recrystallized at least once before use.

Because oxalic acid or oxalates exert a marked bleaching effect on the color produced by hydrogen peroxide,[1] the solution of this salt cannot be used directly as a standard. It can be dissolved in water and the TiO_2 precipitated and brought into solution by fusion with pyrosulphate, or the oxalic acid can be destroyed by ammonium sulphate according to the method of Thornton and Roseman.[2]

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[1] Hillebrand-Lundell, p. 145; Kolthoff-Furman, Vol. Anal., p. 80.

[2] Yoe's suggestion of the use of ferro-titanium for the standardization (Colorimetry, p. 378) is entirely unsuited for rock analysis. Even for steels it would be best to use some definite titanium compound, such as one of those recommended here or by Thornton. Thornton (personal communication) suggests "titanox," a paint composed of TiO_2 and $BaSO_4$, as a standardizer (Titanium, p. 66).

[3] H. E. Merwin, Amer. Jour. Sci., **28**, p. 119, 1909.

[4] Cf. Rosenheim and Schutte, Zs. Anorg. Chem., **26**, p. 252, 1901.

By the first method 2.22 grams of the potassium titanium oxalate is dissolved in 200 c.c. of water containing a little sulphuric acid, with the aid of a gentle heat. The titanium is precipitated as metatitanic acid by *boiling*[3] the liquid and adding an excess of ammonia. The precipitate is collected on a large filter, washed a few times with hot water, and is ignited in a large platinum crucible. It is then brought into solution by prolonged fusion with potassium pyrosulphate, the cake being dissolved in hot water containing sulphuric acid. In this way potassium sulphate is introduced into the solution, so that its bleaching effect is much like that of the test solution.

The liquid is then diluted to 500 c.c., enough concentrated sulphuric acid being added so that the final solution contains at least 5 per cent of this by volume. This addition is necessary, partly to prevent hydrolysis on standing and also to lessen the bleaching effect of the alkali sulphate. The standard will therefore contain approximately 0.01 gram of TiO_2 in 10 c.c., but it must be exactly standardized by precipitating two or three portions of 50 c.c., diluted to 200 c.c., with ammonia while boiling, or, better, with cupferron (p. 200).[4] The precipitated metatitanic acid is ignited and weighed as TiO_2. The mean of the two or three is used for calculating the TiO_2 content of the standard. It is not necessary to make a correction for iron if the pure, recrystallized salt is used.

The procedure of Thornton and Roseman is as follows. It has the great advantage of doing away with the tedious fusion with pyrosulphate, and is to be used if a Kjeldahl flask is available. About 4.5 grams of recrystallized potassium titanium oxalate, which contains about 1 gram of TiO_2, is mixed with 8 grams of ammonium sulphate and the mixture is placed in a 250-c.c. Kjeldahl flask. Fifty cubic centimeters of concentrated sulphuric acid is added and heat is applied gradually. This operation must be conducted under the hood. There is a little foaming at first, but the liquid soon becomes quiet. The liquid is finally brought to a boil and is maintained so for ten minutes or more. The authors state that the whole heating operation can be completed in twenty minutes, but it is as well to take a somewhat longer time, so as to insure the complete decomposition of the oxalic acid. The liquid is allowed to cool and is poured into 800 c.c. of water, which, after cooling, is poured into a 1000-c.c. measuring flask and diluted to the mark. The final liquid is filtered into a large well-stoppered Pyrex bottle, and the TiO_2 content is determined as above, best with cupferron, in three 50-c.c. portions. The complete destruction of oxalate may be tested by adding a drop of potassium permanganate solution to a small quantity of the liquid. There should be no decolorization of the permanganate. Comparative tests by the authors showed excellent agreement with a standard prepared from potassium fluotitanate.

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[1] In this our experience differs from that of R. D. Hall (Jour. Am. Chem. Soc., **26**, p. 1241, 1904), who observed that the intensity of color of peroxidized titanium solutions is bleached by citric acid, but was not noticeably affected by oxalic or tartaric acid.

[2] Thornton and Roseman, Am. Jour. Sci., **20**, p. 14, 1930.

[3] In the cold ammonia forms a gelatinous hydroxide, which is very difficult to wash.

[4] Thornton (Titanium, p. 128) prefers to precipitate by Gooch's method (p. 197) or by cupferron, because the precipitate by ammonia is apt to occlude alkali. According to Hillebrand–Lundell (p. 458) there is little error from this source.

If potassium fluotitanate is used,[1] the salt should be recrystallized from boiling water containing a little hydrofluoric acid in the platinum basin, and dried at not over 105°. It is then the monohydrate, $K_2TiF_6.H_2O$, and contains titanium equivalent to 30.95 per cent of TiO_2. It is completely dehydrated at 150° C., when it contains titanium equivalent to 33.28 per cent of TiO_2. If the monohydrate is used, 3.25 grams, and if the anhydrous salt, 3.00 grams, is weighed into a platinum basin and 100 c.c. of 1:1 sulphuric acid added. This is evaporated until white fumes of SO_3 escape freely, when the contents are allowed to cool, the sides of the basin washed down, and the operation is repeated at least once, and better twice, to insure the *complete expulsion of hydrofluoric acid.*

When cool the residue in the dish is mixed with 10 c.c. of 1:1 sulphuric acid and then with water, enough sulphuric acid being added to make at least 5 per cent by volume of the final solution. When cold the liquid is diluted to 1000 c.c. in a measuring flask. This solution must be exactly standardized on three portions as described above.

The purest titanium dioxide may also be used. A quantity of 0.5 gram of this is fused for about one hour with much potassium pyrosulphate. The cake is dissolved in hot water containing sulphuric acid, filtered, and any undissolved TiO_2 is fused with more pyrosulphate until solution is complete. The final volume, containing at least 5 per cent of sulphuric acid, is 500 c.c. This must be standardized as described above.

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[1] Cf. Hillebrand–Lundell, p. 458.

Dunnington[1] uses ammonium pyrosulphate for the fusion of TiO_2, but potassium pyrosulphate is preferable because the standard solution thus obtained resembles the test solution, and alkali sulphates have a marked bleaching effect on the colorimetric method, as will be discussed later. It is best not to bring the titanium dioxide into solution by evaporation with sulphuric and hydrofluoric acids (as was suggested in the previous edition), because of the difficulty in completely expelling the hydrofluoric acid.

As titanium dioxide is apt to contain some iron this may be determined by the sulphocyanate colorimetric method, as suggested by Thornton, but it is scarcely worth while for ordinary work, and, as pointed out by Thornton, is not necessary if the solution has been standardized by hydrolysis of the acetate in presence of sulphurous acid.

The stopper of the bottle containing the standard solution should be greased with vaseline and the portions used for the analysis are to be withdrawn by a pipette, never by pouring. The solution keeps well if it is strongly acid, from 5 to 10 per cent of sulphuric acid, but its titanium content should be determined from time to time.

Water.—Only pure, distilled water is to be used throughout the analysis, and it will be understood that this is referred to whenever water is mentioned in the analytical procedures in this book. The use of impure water will vitiate the results of any analysis, and too great precautions cannot be taken to provide for an ample supply of pure, distilled water, and for its proper storage. These important points are neglected only too frequently. The water, after distillation, should be stored in large bottles[2] of some resistance glass (preferably Pyrex), and should be used as fresh as may be practicable.

Zinc Oxide (1 ounce).—A little of this may be needed for the rarely executed determination of fluorine.

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[1] Cf. Thornton, Titanium, p. 128.

[2] Some chemists prefer to keep the supply of distilled water in covered porcelain pails, with a faucet.

PART III

THE SAMPLE

1. Selection in the Field

Since the object of the chemical analysis of rocks is to ascertain the chemical composition of a body of rock, it is of fundamental importance that the specimen selected for analysis and the material analyzed, should be truly representative of the mass under investigation.

If, for instance, an igneous mass is not uniform in character, and the specimen is selected from some extreme phase of variation, it is obvious that an analysis of this will not give a just idea of the character of the mass as a whole. Again, in analyzing a diorite, for instance, the specimen may be so small or selected with so little care that it contains a larger proportion of hornblende, let us say, than the average of the mass; or the specimen of quartz-porphyry may carry only a few phenocrysts, and a disproportionate amount of ground-mass. It is evident that an analysis made on such inadequate material, however skilfully it may be executed, cannot represent the true composition of the rock-mass. It is seen, therefore, that the proper selection of the material for analysis depends on three factors: the selection of the representative specimen in the field, the amount of material taken, and the proper sampling of this for use in making the analysis.

Although the selection in the field is quite apart from the laboratory processes, yet its importance is so great as a preliminary to the analysis that it demands some discussion. This is the more called for since the petrologist will usually collect his own material, for analysis either by himself or by others, and, as has been said elsewhere, "the evidence is conclusive that the specimen analyzed has often been collected with no reference to this point, this fact greatly diminishing the value of the analytical work afterward expended on it." In selecting a representative specimen in the field attention must be paid to two points: the uniformity of the mass, especially in regard to the mineral composition as well as to texture, and the freshness of the rock.

Uniformity of the Rock-mass.[1]—If the igneous mass is sensibly uniform throughout its extent, as is true in the majority of cases, specimens should be taken from several parts, when possible, in order to test the uniformity with the microscope. For an analysis representing the composition of such a uniform body of igneous rock, either portions of several specimens from different parts may be mixed, or the analysis may be made on a single specimen, which is considered to be representative of the whole in the judgment of the petrographer, as decided in the field and as confirmed by the microscope.

As to the former procedure it may be said that no decisive check of one's results will be possible in the future, and that it is by no means certain that a mixture of several specimens really represents the composition of the whole better than does a single specimen which has been carefully selected with this object in view.

Furthermore, the *analysis of a single specimen can be correlated with its mode,* or quantitative mineral composition, as determined by the microscope in thin section. To put it briefly, the analysis should represent the chemical composition of a specimen and the specimen should represent the composition of the rock-mass, in order that petrology and petrography, both in their broader and narrower aspects, may safely avail themselves of the data.[2]

Many examples of remarkably great uniformity in chemical composition of great bodies of igneous rock, both plutonic masses and effusive flows of the same volcano, might be cited. Examples that have come under the attention of the author are: the granite of Quincy, Massachusetts;[3] the syenite of Plauen, Saxony;[4] the hyalodacite of Santorini;[5] the andesite of Montagne Pelée;[6] the rhyolite of Katmai;[7] and Dr. Shepherd has kindly shown an especially striking series of analyses made by him of the obsidians of Great and Little Glass Mountains, Modoc County, California. In all these and in many other cases analyses of specimens of rocks from different parts of the same body are so similar that they might well be satisfactory duplicates, although they have been made by different chemists in some cases, or in others by the same chemist from different parts of the mass. It should be noted, however, that more examples might be cited of very great diversity in different parts of the mass.

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[1] Cf. Washington, Prof. Paper **99**, p. 12.

[2] The question of the variability of an apparently uniform rock-mass, and the representativeness of a single specimen is briefly discussed in Washington, Prof. Paper **99**, p. 11.

[3] Washington, Am. Jour. Sci., **6**, p. 181, 1898; C. H. Warren, Proc. Am. Acad. Arts and Sci., **49**, p. 227, 1913.

[4] Washington, Am. Jour. Sci., **22**, p. 129, 1906; R. Nacken, Neues Jahrb. Centralbl., 1914, p. 183.

[5] Washington, Cong. Géol. Internat., C. R. *XII*, p. 235, 1913; Bull. Geol. Soc., Am., **37**, p. 378, 1926.

[6] Lacroix, La Montagne Pelée, 1904, p. 527; Shepherd and Merwin, Jour. Geol. **35**, p. 97, 1927.

[7] E. G. Zies, Nat. Geogr. Soc., Contrib. Tech. Papers, **1**, No. 4, p. 57, 1929.

In all, or nearly all, cases, therefore, a single specimen should be selected for analysis after due comparison with others from the same mass and consideration of its representative character. The specimen should be taken, if possible, from a mass of rock in place, and not from loose boulders or talus slopes, unless these are the only sources available and it is definitely known that they come from the mass under investigation.

If the mass is not uniform, but is composed of portions of different characters, such as a composite dike or stock with marginal facies, representative specimens of the different facies should be collected and an analysis made of each, whether the differences be apparently only textural or those due to mineral composition. If in any way feasible, as close an estimate as the conditions allow should be made of the relative thickness, area, or volume of each facies. Although the possibility of doing this depends to a large extent on the conditions of exposure due to the chances of erosion and denudation, yet it is of such importance in the investigation of certain theoretical questions of petrology that special endeavor should be made to arrive at the quantitative relations.

In any case, whether the mass is uniform or composed of several facies, the specimen should be taken, if possible, from some definite locality, one that can be described or named so that it can be readily identified by others, and also one whose accessibility is not likely to be lost through building or other operations. Quarries naturally are especially favorable spots, as fresh specimens are easily obtained, and they are of such a permanent nature as to be readily identified, in most cases, by future investigators. In rapid reconnaissance or exploration one has, of course, mostly to be content with, and thankful for, chance specimens.

Freshness of the Rock.—The action of atmospheric agencies on rocks may vary from the changes to which Merrill[1] attaches the specific term ''alteration,'' in which ''the rock mass as a whole retains its individuality,'' but is changed mineralogically, with the production of secondary minerals, chlorite, sericite, serpentine, limonite, etc., to those embraced under what Merrill calls ''weathering,'' ''involving the destruction of the rock-mass,'' and its ultimate resolution into sands and clays. The mass resulting from such changes, either of alteration or of weathering, can be analyzed by the same methods and with equal facility as can a perfectly fresh rock, but it is evident that the results will not represent the composition of the original magma or unaltered rock body.

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[1] G. P. Merrill, Rocks, Rock-Weathering and Soils, p. 174, 1897. See also: C. R. Van Hise, A Treatise on Metamorphism, U. S. Geol. Survey Mon. **47**, pp. 409–561, 1904; Leith and Mead, Metamorphic Geology, p. 89, 1915; L. V. Pirsson, Rocks and Rock Minerals, pp. 284, 351, 1926.

Although it is true in general that only specimens of fresh (unaltered or unweathered) rock should be chosen for analysis, unless the study of such secondary changes is the object in view, yet it is at times somewhat difficult to decide whether a rock is or is not fresh enough to justify analysis. In general, it may be said that, for the study of igneous rocks, all weathered specimens are to be rejected, that is to say, those in which the rock-mass has been formally broken down. In the case of alteration, specimens should be rejected whose original color is decidedly changed, as where the rock is of a rusty brown through the abundant production of limonite, or green through that of chlorite. Specimens that effervesce with hydrochloric acid, either cold or on warming, or whose vesicles contain calcite or zeolites, are likewise to be shunned.

Specimens should, therefore, be taken (if possible) from the interior of the mass and not from the surface, and portions of specimens from near the surface, where the rock has been exposed to atmospheric agencies, are to be rejected.

In rocks that appear megascopically to be quite fresh, the microscope may reveal the presence of secondary minerals, the products of alteration, as sericite, chlorite, serpentine, or limonite. Although considerable latitude must be left to the judgment of the petrographer in deciding this matter, yet if such minerals are present to any considerable extent, the rock must be regarded as unfit for chemical analysis, unless fresh material is unattainable. This last state of affairs is especially apt to be true of the most basic rocks, such as alnöites, picrites, peridotites, and pyroxenites, which contain a large amount of the easily oxidizable ferrous iron, and of which few perfectly fresh occurrences are known or have been analyzed. For lack of better material, one must often analyze specimens of such rocks that are far from fresh, but the results, while not to be regarded as wholly satisfactory, may yet be of some service.

The results of alteration are usually most clearly shown in the analysis by the figures for H_2O or CO_2, or both. Where these are high the material analyzed must be considered as having been more or less altered, whether this appears in the description or not, with the exception of certain cases mentioned below. While it is impossible to state in exact figures the limits of allowable alteration, until the subject is further studied, it may be held provisionally that H_2O can go up to 2 or 3 per cent and CO_2 to 0.5 per cent, without the rock being considered to be so altered as to seriously affect the value of the analysis. It must also be borne in mind that a rock can be more or less profoundly altered, and yet show comparatively low figures for these two constituents, though this is not often to be expected.

The exceptional cases just referred to consist of rocks composed in part of primary minerals that contain either hydroxyl (as muscovite and biotite), water of crystallization (analcite), or carbon dioxide (cancrinite). With rocks carrying analcite, which is apparently the only zeolite that can exist as a primary mineral, the H_2O may amount to 3 or 4 per cent, and yet the mass be to all appearances perfectly fresh, and in some cases certainly so. Indeed, analcite is now well recognized as a primary mineral in igneous rocks, although secondary analcite occurs more frequently. Highly vitreous lavas, as perlites and tachylites, may contain several per cent of water and yet be perfectly fresh; water often occurs as inclusions, as in the quartz of many granites. Cancrinite-bearing rocks[1] may have more than 1 per cent of CO_2 and yet be quite unaltered, and the cancrinite is primary, although this mineral is often secondary.

The existence of calcite as an undoubtedly primary mineral has not been established as yet, though recently rocks have been described in which its occurrence as such seems probable, if not certain.

In discussing the subject of analyses of altered rocks, we may advert to a phase of the matter which is of some importance. When a rock is not fresh it is sometimes assumed that the original composition can be arrived at by deducting the amounts of H_2O and CO_2 and calculating the remainder to 100 per cent. This assumption is generally quite unwarranted, since the processes of alteration are usually by no means simply the result of the addition of the two substances mentioned. On the contrary, they are complex and produce changes of greater or less magnitude in the proportions of some or all of the constituents. These may be additive, as when calcite is deposited in rocks by percolating waters carrying calcium bicarbonate in solution, or they may be subtractive, as when kaolinization of a feldspar takes place with resultant loss of alkalies and lime. In any case it is almost universally true that the process of rock disintegration affects the proportions of all or nearly all of the chemical constituents, so that the assumption that such is not true is unwarranted by the known facts.

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[1] No cancrinite-bearing lavas are known.

It should be understood that this form of recalculation, however, is quite distinct from "cooking" or "doctoring" the analysis, discussed on page 27.

2. AMOUNT OF MATERIAL

[illegible] 87-105 [illegible]

As has been said above, the representative character of the specimen depends, after proper selection in the field, supplemented by the use of the microscope, upon the amount of material that is taken for pulverization in preparation for the analysis. The weight of the sample that will adequately represent the average of the rock-mass varies with the texture of the rock, and especially with its granularity; that is, the size of its component mineral particles.

It may first be noted that 10 grams of rock powder should be available for the purposes of analysis, and this amount should be increased to 20 or 30 grams if the analysis is to be very complete, since the determination of some of the rarer constituents demands the use of 2 or more grams of powder. Indeed, it is always a wise precaution to have 20 grams on hand, in view of the possible necessity for the duplicate determination of some of the constituents, or even the making of a second complete analysis.

It is often impossible to obtain anything like this amount of material for the analysis of minerals or meteorites, and the analyst must be content with smaller quantities, sometimes much less than a gram of a mineral for the whole analysis. With rocks, on the other hand, there is usually an ample supply, so that the analyst has generally no reason to stint himself. In this way a number of constituents can be easily determined in separate portions, which could only be accomplished by the use of longer and more complex methods if it is necessary to determine them in a single portion.

The texture of rocks varies within such wide limits that it is impossible to give a general rule as to the amount of material that is representative. Much must be left to the judgment of the petrographer. Speaking generally, and almost without exception, the finer grained and less porphyritic the rock, the smaller will be the amount of material necessary to be representative.

Thirty grams of chips or fragments will be ample for very fine-grained, aphanitic, or glassy rocks, as many basalts, trachytes, and obsidians, especially if they are not porphyritic, or very finely so. With more coarsely granular rocks, such as granites, syenites, and diorites, a larger quantity must be taken, depending on the coarseness of the grain. This amount may vary from 50 grams of a medium-grained rock to 100 or even more if the grain is coarse. In some cases, as in pegmatites, the grain may be so large that only a whole hand specimen, or even several kilograms, will adequately represent the true composition. Very exceptionally the crystals may be of such gigantic size that the relative proportions of the various minerals must be estimated from a flat exposure and corresponding portions of the several minerals weighed out, mixed, and sampled. Fortunately, this last will rarely be necessary, and results obtained thus can be regarded as but very rough approximations to the truth.

If the rock is porphyritic, this feature involves the taking of a larger quantity than would be necessary if the grain of the whole were that of the groundmass. If the phenocrysts are very small, only a few millimeters in diameter, and close together, as in many andesites and basalts, 30 grams will be sufficient. As they get larger, and if more widely scattered, more must be taken, from 50 to 100 grams to larger quantities. With porphyritic rocks also, care must be taken that brittle or loosely attached phenocrysts, as of feldspar, quartz, or leucite do not fall out, so as to yield a disproportionate amount of groundmass in the material for analysis.

3. Preparation of the Sample

Sampling.[1]—If the rock is so fine-grained or so slightly porphyritic that only about 50 grams of fragments is considered to be representative, the whole amount, broken up if necessary, may, without sampling, be crushed, sifted, and ground as described below.

If, however, the representative weight is much more than this, say 100 grams or over, the final crushing and grinding of the whole will consume an inordinate amount of time, so that sampling is advisable to obtain the smaller amount needed for an analysis that will be representative.

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[1] Hillebrand–Lundell, p. 47; Mellor, p. 127.

This may be done by breaking up the piece or pieces of rock, if large, with a hammer over a large, clean sheet of paper, until the largest is small enough to put into the steel mortar. The larger fragments, say down to 0.5 cm. in greatest dimension, are crushed, one at a time, to smaller fragments and coarse powder, in the Plattner diamond mortar, and emptied out on the sheet of paper. The whole mass is then well mixed with a steel spatula and shaped into a low cone. This is ''quartered'' with the spatula, and if the quarter is more than about 50 grams, the process is repeated (more than once if necessary) until a proper amount of sample has been obtained.

Methods of Pulverization.—For analysis, the sample of the rock must be reduced to fine powder so that it may be easily and completely decomposed by the reagents used. To accomplish this, one of three methods may be followed.

The first is that formerly used in the laboratory of the U. S. Geological Survey.[1] The rock is first crushed to small fragments and powder by means of a hardened-steel hammer on a hardened-steel plate. The plate is 10 cm. square and 4½ cm. thick. The rock fragment is surrounded by a steel ring, 6 cm. in internal diameter and 2 cm. high, intended to prevent the flying and loss of fragments. After reduction in this way to small particles and powder, the whole is ground down by hand in an agate mortar, in small portions at a time. As will be seen later, the great defect in this method is the unavoidable and probably very serious loss of small fragments and dust, both in the preliminary crushing, which the ring does not wholly prevent, and especially in the grinding.

The second method is that described by Hillebrand as the one now in use in the Survey laboratory.[2] The rock, broken into small pieces, is crushed in an Ellis mortar (p. 48), the pestle being of the knob type. In this it is crushed to a powder fine enough for most of the portions used for the analysis. When the decomposition calls for a finer powder, small portions are ground down by hand in an agate mortar; the material may be sifted. The use of mechanical grinders has been abandoned in the Survey laboratory.

In the third method, which is the one the author has followed for many years, the rock, broken into small pieces, is crushed in a hardened-steel Ellis mortar, much as in the Survey method, but the pestle is without a knob and flat at the top, and a hammer is used.

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[1] Hillebrand, Bull. **176**, p. 31.

[2] Hillebrand, Bull. **700**, p. 58; Hillebrand–Lundell, p. 670.

After the first crushing of the whole, it is sifted through silk bolting-cloth, the oversize being again crushed and sifted, and this operation is repeated until only a gram or so of oversize portion remains, which is ground by hand in an agate mortar.

In considering the relative merits of these methods, two factors must be discussed, as on them depends the attainment of the object in view, namely, the production of a rock powder that will represent as accurately as possible the composition of the rock specimen taken. These two factors are: contamination from the mortars, and the loss caused by the flying of fragments and dust.

Contamination by iron derived from the steel mortar and pestle or plate and hammer is much more serious than that by silica derived from the agate. This is because, in igneous rocks silica is present in much greater amount than are iron oxides, and the introduction of metallic iron would affect the ratio of ferrous to ferric iron. Furthermore, the author believes that the liability to contamination by iron is more likely to be relatively greater than that by silica, in spite of Hempel's experiments.[1] The first hardened steel ''diamond'' mortar (not made by Ellis) used by the author shows greater signs of abrasion, though it is but slight, than his small agate mortar, although both were in use concomitantly for the same period of about thirty years, the agate mortar indeed, some fifteen years longer.

If the steel has been properly hardened, and the crushing is done by strictly vertical blows, without rubbing, the contamination by iron through abrasion is slight, so slight indeed, as to be negligible.[2] There is, however, a very slight contamination, especially on oft-repeated crushing, even though this is properly done, as Hillebrand shows. In any case, this source of error would seem to be unavoidable. The rock must be reduced to powder for analysis, and hardened steel is at present the only practicable material of which to make mortars (p. 48).

It is essential, and most important to remember, that there must be absolutely *no rubbing or rotary motion of the pestle* during the crushing, because such motion would inevitably introduce iron into the specimen.[3]

Contamination by silica from the agate is very slight. It is entirely negligible if the grinding is not long-continued. Experiments by E. T.

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[1] W. Hempel, Zs. Angew. Chem., p. 843, 1901. Cf. Hillebrand, Bull. **700,** p. 64; Hillebrand–Lundell, p. 675.

[2] Cf. Hillebrand, Bull. **700,** p. 59, note; Hillebrand–Lundell, p. 671.

[3] Hillebrand, Bull. **700,** p. 58; Hillebrand–Lundell, p. 670.

Allen,[1] in which 200 grams of quartz sand were ground for 19.5 hours in an agate mortar, showed a loss by abrasion to the pestle and mortar amounting to 0.145 per cent of the weight of the sand. With small amounts and with only a few minutes' grinding the contamination is certainly negligible.[2]

In the opinion of the author, mechanical grinders should not be used. Apart from the cost, the danger of contamination by oil is always present, in spite of safeguards. Furthermore, the long-continued grinding is not only unnecessary for the whole of the sample and takes much time, but it introduces silica from the mortar, leads to error by the oxidation of the ferrous oxide, and increases the absorption of moisture by the fine powder.[3] On the other hand, water may be expelled from hydrated minerals [4] and carbon dioxide from calcite [5] by long-continued grinding. The sole advantage is the attainment of greater homogeneity of the powder, which is unnecessary and is more than offset by the disadvantages. The use of mechanical grinders has been abandoned by the chemists of the U. S. Geological Survey and of the Geophysical Laboratory (for rocks), for the reasons just mentioned.

If the rock is homogeneous and aphanitic, like an obsidian or a dense, non-porphyritic basalt, the loss of fragments or dust in the crushing or the grinding of a coarse powder will not affect materially the composition of the final material. If, however, the rock is coarse-grained or porphyritic the change in composition may be serious. The tough minerals, such as pyroxene or amphibole, crush with difficulty, and so tend to accumulate in the powder with successive crushings and siftings. The products of the first crushings will therefore be richer in the more brittle, salic minerals, such as feldspar and quartz. To some extent this is offset by the tendency of the tough grains to fly off. But these will carry with them some adherent brittle (and mostly salic) material. The loss of fine dust blown or wafted away during the crushing and sifting is also a factor to be taken into account. This will, almost certainly, be made up of more of the salic minerals (quartz and feldspars) and glass[1] than of those which are femic, high in iron and magnesia, because of the greater brittleness and lower specific gravity of the former.

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[1] Hillebrand, Bull. **700,** p. 63; Hillebrand–Lundell, p. 675.

[2] The estimate of about 0.3 per cent of silica introduced, as given by M. C. Connor (XII Cong. Geol. Int. C. R., p. 885, 1914) is surely higher than in my experience, and is probably accounted for by Connor's analyzing corundum-bearing rocks.

[3] Cf. Day and Allen, Carnegie Pub. No. **31,** p. 56, 1905; Hillebrand, Bull. **700,** p. 69; Hillebrand–Lundell, p. 682. E. T. Allen has found that optical glasses, on prolonged grinding in a mechanical mortar, may absorb as much as 1 per cent of water. (Personal communication.)

[4] Hillebrand, Bull. **700,** p. 70; Hillebrand–Lundell, p. 682.

[5] Johnston and Niggli, Jour. Geol., **21,** p. 614, 1913.

It is not known from experiment in which direction these different factors tend, as the few researches regarding the effects of crushing and grinding that have been made are inconclusive, indicating only the influence of the greater hardness of quartz over feldspar.[2] The tendency from these causes in either direction would probably be irregular and depend largely on the mineral and textural characters of the rock. On the whole, however, it appears to be probable that, in general, the loss of dust would outweigh that of the loss by flying of the tough grains, so that, probably, the final rock powder as analyzed is slightly more femic than the rock itself in the case of all but very fine-grained or aphanitic rocks.

In the first method of preparing the sample of powder mentioned above, contamination by iron would probably be notable and, what is a still more serious matter, the loss by flying fragments, and that of dust, is apt to be so great that the method should not be used.[3]

The second method involves prolonged crushing in the steel mortar to bring the whole powder to a state of fineness (something like 40 meshes to the centimeter) that will permit ready attack by sodium carbonate. This renders the sample liable to contamination by iron in direct ratio to the time expended in crushing. If the crushing is not carried out to this extent, but if the powder yielded by the steel mortar is ground down in agate, without sifting, loss and consequent change in composition by flying fragments or dust would be inevitable, as is evident from the considerations above and as can be easily verified.

In the third method the crushing in the steel mortar is briefer than in the second, because the larger fragments are separated from the powder by sifting and thus in the subsequent re-crushings are not protected by the cushioning effect of the powder, and are therefore more quickly pulverized.[4] If the sifting is carried out in a place free from drafts, the sieve being held close above the paper below, and the sifting is gentle and at frequent intervals, the third method, as described below, produces a negligible amount of fine dust. Even this loss can be entirely done away with by using a double glass box (p. 53). The grinding of the final portion in agate causes but a slight and negligible loss of the tougher minerals.

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[1] The very ferruginous glass of some basalts must also be considered.

[2] S. Zaleski, Tsch. Min. Pet. Mitth., **13**, p. 343, 1895; I. A. Williams, Amer. Geol., **35**, p. 38, 1905.

[3] It is not now used in the laboratory of the U. S. Geological Survey.

[4] No indications have been found, by the author, of the presence of metallic iron when the rock powder, obtained by his method, is ground under water in an agate mortar, as described by Hillebrand (Bull. **700**, p. 59); Hillebrand–Lundell, p. 671); the samples of rocks analyzed included many different kinds.

The objection against the use of silk bolting-cloth formerly raised by Hillebrand,[1] is of little moment. The danger of contamination by particles of silk, and hence of error in the determination of FeO, is more theoretical than real. The error introduced from this source would certainly be far less than the errors inherent in the method and procedure themselves. If the crushed material from the steel mortar is only shaken, not rubbed through the sieve (the German ''beuteln''), only a negligible weight of silk in all would pass into and be distributed through the 10, 20, or more grams of rock powder, of which but one-half a gram is taken for the FeO determination. It is certain that the reducing action of the extremely small weight of organic substance thus introduced would be much less than that necessary to decolorize a single drop of the permanganate solution, and hence would be entirely negligible, even for very accurate work.

Metal sieves should not be used for the analysis of rocks, as they may introduce contamination or complication in accurate work. In the analysis of silicate minerals they are, of course, quite out of the question.

It is therefore held that the third method is the one least liable to error and the one that will furnish material for the analysis that will more closely represent the original rock than the second, and still more than the first. It may now be described in detail.

Pulverization of the Sample.—The whole amount of the sample that is representative of the rock-mass is reduced to small fragments, if the amount of material is small, by breaking up with a small hardened hammer on the small steel plate (p. 54) or on the top of the steel pestle which is placed in position in the mortar. Care must be taken to avoid the flying-off of fragments. *Wrapping the rock in paper* to prevent this, as is sometimes done,[2] *is absolutely inadmissible,* because it is impossible to free the fragments entirely from adhering paper, and the organic matter thus introduced may lead to serious error, especially in the determinations of FeO and H_2O.

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[1] Hillebrand, Bull. **148**, p. 23; Bull. **176**, p. 32. In Bull. **422**, p. 51, and Bull. **700**, p. 58 (Hillebrand–Lundell, p. 670), Hillebrand advocates its use.

[2] Dittrich, p. 2; Jannasch, p. 298; Mellor, p. 120.

The pieces of rock are held in the dry fingers and cracked by sharp, quick blows with a light hammer, and the pieces so obtained are cracked again. The largest of the fragments finally obtained must be small enough to drop easily into the mortar, and all of them, with any resulting small grains and powder, are placed on a clean sheet of white, smooth paper, like that used for typewriting.

One of the small fragments of rock is then placed in the steel mortar, which should rest on a firm, solid support, preferably an upright, short column of wood, resting on the floor, and is partially crushed by a dozen or so sharp but gentle blows of a light (half-pound) hammer. The pestle is removed and placed on the sheet of paper, and the contents of the mortar are dropped into the glass sieve-box (p. 53). A few gentle taps of the base of the mortar against the cylinder assist in removing the last portions of adhering powder from the cavity. It is well to break up any coherent lumps of fine powder in the glass box by gentle pressure with the pestle, as this aids in the subsequent sifting.

It is essential, as pointed out above, that there must be *no rubbing or grinding motion during the crushing.* The pestle and cylinder are held together firmly in the fingers of the left hand, so that there may be no rotary motion, and the blows of the small hammer should be gentle and strictly vertical. Any grinding of the pestle against the sides of the cylinder or rotation on the rock powder will surely introduce some iron through the wearing of the metal surfaces.

The mortar cylinder should not be filled more than to the depth of from 3 to 5 mm. at a time, and it is not necessary nor advisable to crush all of the rock to fine powder at this stage, as the fine powder has a *cushioning effect* on the larger fragments. It is therefore useless to strike the pestle with the hammer more than one or two dozen times. Care should be taken that the cylinder is placed vertically in the base before any fresh material is placed in it, and that the pestle is also inserted in a strictly vertical position. Lack of attention to these points gives rise to the danger of small chips or shavings of steel being cut off and falling into the rock powder.

The whole of the fragments and powder produced by the first successive crushings are thus collected in the glass sieve-box. A piece of silk bolting-cloth of 100-mesh (p. 53), about 10 or 12 cm. square, is stretched over its mouth and held firmly in place by the brass ring (or section of clock-spring) which is slipped over it. If the double form is used the second box is put in place.

The sieve is then held upside down over another sheet of white, hard-calendered paper,[1] about 300 by 400 cm. (12 x 16 inches), *a short distance above it,* and gently shaken from side to side. The paper is, of course, not needed if the double box is used. This operation should be conducted as *gently* as is consistent with proper effectiveness, and in a *place free from drafts,* to avoid loss of dust.

When no more powder falls through, the brass ring and the gauze are removed, and the contents of the box are poured out on the first sheet of paper. The whole process of crushing in the steel mortar is then gone through with on this material, exactly as before, and it is again sifted. The residue from the second sifting is again treated, and if necessary the process is repeated until only a small amount (1 gram or less) of coarse powder is left in the glass box, too coarse to pass through the gauze. This final portion is then ground down by hand in the 9-cm. agate mortar in small portions at a time, the different portions as they are ground being scattered over different parts of the low heap of powder on the sheet of paper or in the second box. Unless the amount of material to be crushed is very large, or the rock is extremely tough, four to six successive crushings will be all that will be needed. The final grinding of the last small lot of powder *must never be omitted,* as this consists of the tougher minerals of the rock, and if it were thrown away, the rock powder would not represent the specimen of rock.

When the whole is thus passed through the sieve, the powder is *very thoroughly mixed.* This is best accomplished on the paper by tilting up successively the ends and the sides of the paper until the mass is at the center. One end of the sheet is then raised gently until the heap of powder is lifted and turned over and slid toward the other end. It is essential to proper mixing that the mass of powder should not only slide down, but that it should actually be turned over. This is repeated many times, not only from end to end, but from side to side, with an occasional oblique roll. A platinum spatula may also be used to mix the powder, but care must be taken that none of the paper surface is rubbed off. The procedure described above is to be preferred. When it is considered that the powder is thoroughly mixed, it is not an undue precaution to roll it over in different directions several times more. The powder may also be quickly and thoroughly mixed by putting it again in the box and sifting it through a somewhat coarser (50-mesh) bolting-cloth. It is best to use the double box, as thus no fine dust is lost.

[1] The sheets used by botanists for herbaria will be found to serve admirably.

After thorough mixing, the powder is poured into a specimen tube. For amounts of 20 to 30 grams, one of 6 x ⅞ or 5 x ⅝ inches will answer, while one of 4 x ½ inches will hold about 10 grams of rock powder. The tube used must have been carefully cleaned, inside and out, by washing with distilled water, (it is needless to use alcohol), and is then thoroughly dried. This is accomplished by gently heating the tube over a low Bunsen flame, the moist air being at the same time sucked out through a piece of glass tubing attached to the suction-pump. The tube must be perfectly cool before the powder is introduced, and is to be closed with a smooth, well-fitting cork, on the top of which the number of the specimen is written in ink. The number, name, and locality of the specimen should also be written on a small label pasted on the side of the tube.

In order to avoid the possibility of rusting, the steel mortar *should be cleaned,* a stiff brush and a dry cloth being used, *immediately after the preparation of the sample,* and placed in a tightly-closed box. The bolting-cloth may be used many times, but it must be very thoroughly dusted free from any trace of rock powder after each operation. For very accurate work a fresh piece is to be taken. The glass box or boxes and the brass ring are also to be cleaned.

It is of the utmost importance that *all of the sample* which is prepared for the steel mortar, either the chips, if the amount of material is small, or that obtained by quartering if it is large, must be pulverized in the agate mortar. If it is only partially pulverized and the last portions are rejected, it is clear that the powder so obtained will not represent the average composition of the rock. The rock-forming minerals differ widely in brittleness, so that the portions pulverized first will have a content higher than the average in particles of the more easily pulverizable minerals, as quartz, feldspar, and feldspathoids, whereas the last portion will be especially rich in the tougher minerals, pyroxene, hornblende, and the micas.[1] The micas, above all, are difficult to pulverize completely either in the steel or agate mortar, on account of their ready cleavage and flexibility, but the thinness of the flakes renders mica quite easy of attack by the reagents used. If mica is present in any quantity it is necessary to see that the flakes are well distributed through the powder.

The analysis should always be carried out on air-dry powder, as specially dried powder invariably readsorbs some or all of the lost moisture by exposure to the air during the weighing and whenever the tube is opened, or even if it be closed.[1] This absorption of water is the greater the finer the powder, and the amount of water thus absorbed has been shown by Day and Allen[2] to be of the same order of magnitude as that of the "hygroscopic" water observed in the analyses of feldspars and many rocks free from hydrated minerals. The preparation of the sample should, therefore, be undertaken on a dry day, never during rain or wet weather.

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[1] Some data are given by I. A. Williams, Amer. Geol., **35**, p. 38, 1905.

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[1] Cf. Hillebrand, Bull. **700**, p. 71; Hillebrand-Lundell, p. 684.

[2] Day and Allen, Carnegie Inst. Publ. **31**, p. 57, 1905; Am. Jour. Sci., **19**, p. 127, 1905.

PART IV

OPERATIONS

1. PRELIMINARY OBSERVATIONS

In the chemical laboratory, above all places, cleanliness is highly important. The analyst must be scrupulously particular about the freedom of the laboratory from dust and dirt, and about the cleanliness of his apparatus. No matter how clean the laboratory may be, all vessels the contents of which are to stand for more than a short time, and especially over night, must be covered to prevent the entrance of dust.[1] In prolonged evaporations it is well to protect the liquid by a large pane of glass or a Meyer's evaporating funnel held sloping above the basin by a clamp and support.

The deposit of ammonium salts that accumulates on the bottles standing on the shelves is not only unsightly, but is a constantly possible source of contamination, especially dangerous in the determination of potash. The bottles should therefore be wiped off every now and then with a damp cloth, and the work-bench should also be washed occasionally.

Every glass utensil or other soiled piece of apparatus should be washed clean [2] and wiped dry immediately after its use, and put away in its proper place. This applies especially to beakers. By conforming to this rule soiled vessels will not accumulate, and there will be no danger that they be put away and used inadvertently instead of clean ones.

A clean beaker is to be used to receive a filtrate, even when this is to be rejected, to permit the recovery of the precipitate if it passes through the filter or if the latter breaks. Before using a clean beaker or flask, it should be rinsed out with a little distilled water from the wash-bottle. In volumetric or colorimetric work the burette should be rinsed out with a little of the solution to be placed in it, even if it is apparently dry.

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[1] A beaker is covered with a watch-glass, of a size so that the edge *projects about 2 cm.* around the beaker, and is always to be placed *convex side down.* A flask is best covered with a small beaker, turned upside down.

[2] The cleaning of glass vessels is discussed by Mellor, p. 36, and by Kolthoff–Furman, Vol. Anal., **2**, p. 3.

The student must shun all slovenly manipulation, such as spilling liquids or solid reagents on the work-bench, or letting liquids drip when pouring from the bottle. Tobacco ashes are a source of danger. The wearing of an apron in making a quantitative analysis is to be deprecated, as tending to confirm one in slovenly habits. If the analyst is liable to drop acids on his clothes he is more than liable to spill some of the solutions he is analyzing.

Every beaker, flask, crucible, or other receptacle that contains a precipitate or filtrate in the course of the analysis and that has to be laid aside temporarily should be clearly labeled with the number of the analysis and the name of the substance. Otherwise, confusion or uncertainty is almost sure to follow, especially if a complicated analysis or a series of analyses is in progress. This labeling can be done by placing a piece of paper with the requisite data on the cover glass [1] or by writing on the spot of ground glass on the side of the beaker or flask.

The beginner has a marked tendency to overdo in many details of the analysis. This excess of zeal is often expressed by using utensils of sizes much larger than are needed, by using inordinate amounts of wash-water, by igniting precipitates for a much longer time than is necessary, or using a much too large or high Bunsen or Meker burner flame. This megalistic [2] tendency is so pronounced and so prevalent that the beginner in analysis should be specially on his guard against it. It is to be discouraged because it not only lengthens the time needed for the analysis, but, what is more serious, it tends to lessen the accuracy of the work in many ways.

The beginner should take full notes during the progress of his first analyses, until the various methods become familiar, and even then all occurrences or manifestations out of the ordinary are to be recorded. The details of all the calculations are to be recorded in the notebook for future reference. It may sometimes happen that an apparent analytical error or an unsatisfactory summation is merely due to a slip in arithmetic, and a re-examination of the recorded weights and calculations may obviate the necessity of a duplicate determination or analysis.

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[1] It is convenient to keep at hand a small basin with squares (about 1 inch) of white cardboard. This is a good use for old notices of meetings and of weddings and Christmas cards. Each label is to be kept with the precipitate of the portion of the constituents as it passes through successive operations. A glass-marking pencil is useful. This may be applied to the smooth surface of the glass.

[2] This word is coined in analogy with optimistic, pessimistic, altruistic, etc., and means doing things in a big way. It seems not to be in the dictionaries, but it is useful, and might well be.

In rock analysis a preliminary qualitative examination is seldom, if ever, necessary. The microscope will often serve the purpose. But if not, and if the presence of some unusual substance is suspected or is thought to be probable, it is better, as Hillebrand remarks, to assume its presence and conduct the quantitative analysis on this assumption. This will be time saved in the end, even if the result is merely to prove the absence of the suspected body, which in itself may be a fact of interest. In such cases, it is well to test by qualitative methods the character of the weighed precipitate to make certain whether it is really the substance in question or not.

Before beginning an analysis the student should see that the balance is correctly adjusted, and that all the necessary apparatus and reagents are at hand, so that the work may proceed without interruption. It will be well to read the whole of the description of each of the various operations and methods before beginning their execution, as some information may be given at the end which is essential to the proper procedure.

As illustrative of the precautions that must be taken in highly accurate work, it may be of interest to the student to read Richards' discussion of the "Methods Used in Precise Chemical Investigation."[1]

2. Sources of Operative Errors

The distinction between errors that are incidental to operations and those that are inherent in the methods used will be discussed later (p. 136). It may be useful here to give a list of those sources of error that are connected with the various operations which are more serious in their consequences or which may be most often met with by the student, and which should be more particularly guarded against.[2] The precautions that may be taken against some of them are given in connection with the description of the various operations.

This list is so long and formidable in appearance that the beginner may be disheartened by the prospect of continuous vigilance that confronts him. For his encouragement it may be said that their aggregate number is more serious in seeming than are in reality the occurrence or possible consequences of many of them. The only ones that are really inexcusable at the beginner's stage are those arising from carelessness, and these may soon be overcome by the attentive and conscientious student, who not only follows the conditions and precautions mentioned in the various descriptions of operations and methods, but who also looks upon the analytical work with intelligent interest, and consequently "learns nothing more than to follow directions." To such a worker the very sources of error themselves are of interest, stimulating him to constant attention, and lending to the progress of the analysis an element of interest and something akin to excitement, which it would lack if every operation and method were wholly free from possible sources of error. It should be remembered that this list is by no means exhaustive.

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[1] T. W. Richards, Determinations of Atomic Weights, Carnegie Institution Pub. **125**, p. 97, 1910.

[2] Mellor (p. 259) gives a similar but shorter list.

Sampling.—Correct sampling is of fundamental importance, but this must be considered as a preliminary to the analysis.

Unfavorable Conditions.—The laboratory may be in a dusty location, or not kept in a properly clean and neat condition; the laboratory air may be contaminated by fumes; the ceiling may be of such character or in such condition as to drop particles into vessels beneath; machinery in motion may disturb balance readings; a window facing the sun, or some other source of heat, may affect the balance; the air may be so damp that powders or objects to be weighed absorb a disturbing amount of moisture; the exterior light surroundings may be such (brick walls or foliage) as to affect colorimetric readings; the attention may be distracted by interruptions or noise.

Personal Equation.—There may be personal peculiarities in the reading of burettes and other instruments that lead to constantly high or low results; there may be a peculiarity in color perception that tends to high or low estimates in colorimetric determinations; one eye may perceive colors differently from the other,[1] or the eye may be fatigued; impatience may lead to the undue hastening or shortening of operations;[2] overwork may cause fatigue and consequently lead to many opportunities for error; the need for quickly attained results may cause errors of many kinds;[3] the analyst may not be in good health.

Apparatus.—The balance may not be properly adjusted; one

[1] Cf. Yoe, Colorimetry, p. 83.

[2] This might more properly come under the head of carelessness.

[3] This is especially true of industrial and commercial analyses.

arm may have been lengthened by heating from a window, etc.; the zero-point may not be known and it may be distant from the center of the scale; the weights may not be correct; the measuring flasks and burettes may not be consistent with each other; the glass of which the beakers are made may be readily attacked by reagents.

Impure Reagents.—The impurities found in reagents are of great variety and some of them quite unexpected. They have been discussed on page 54, and should be guarded against by appropriate testing of the stock reagent.

Standard Solutions.—The standard solutions of permanganate, titanium, and manganese are liable to change and deterioration with lapse of time; they may change by evaporation through opening the bottle or pouring them out; their titer may be increased by not shaking the bottle previous to use, or lessened by moisture in the burette.

Numerical Errors.—The position of the rider on the beam, the weights, the position of the meniscus in the burette, may be incorrectly read and set down; an incorrect factor or an incorrect figure from a table may be used in the calculations; arithmetical mistakes may be made in the calculations; the summation of the results of the analysis may be incorrect.

General Sources.—Volumes may not be corrected for temperature conditions; platinum crucibles may lose weight on ignition; liquids may be contaminated by solution of the material of the containing vessel; precipitates may be contaminated by other substances that are carried down with them; liquids or solids may be contaminated by absorption of fumes or gases (as carbon dioxide or ammonia) from the atmosphere; sulphur may be introduced from the burner gas or from rubber stoppers; platinum may be introduced during fusion in crucibles or evaporation in basins of this metal; copper may be introduced from copper vessels.

Inexperience.—Errors due to this source may be very serious, but they are generally less harmful than those caused by carelessness, and they should be overcome with practice and attention.

The most common and persistent source of error due to inexperience is the tendency to bigness and the overdoing of things. The use of vessels of too large a size, such as beakers, adds to the difficulties of manipulation, increases the volumes of wash-water and other liquids, tends to the over-washing of precipitates, and increases the time taken for the analysis; the use of too large filters leads to the over-washing of precipitates and the under-washing of the filter; the volumes of wash liquids or the amounts of precipitants are easily made much larger than is needed or desirable, and this increases the chances of error in many ways; the use of too large flames in ignition,[1] may lead to the reduction of the ignited substance or loss by drafts in the crucible; the over-washing of precipitates leads to their partial solution and to too low results; too prolonged ignition may cause undue loss of weight of the crucible, and always loses time.

Insufficient washing, or cessation of ignition before constant weight has been attained, leads to too high results; improper position of the crucible as regards the flame, especially that of a blast, may cause loss; the loss of molten substances by spattering, such as of the carbonate fusion, or of the pyrosulphate fusion by spattering or by "creeping," will cause low results.

Among other sources of error are the reading of a Mohr's burette before the liquid has run down the wall; the loss of precipitate by "creeping" up the sides of a beaker or funnel; the incomplete removal of a precipitate from the sides of a beaker; loss by effervescence on the addition of acids to carbonates (as in the solution of the carbonate cake) or that of strong ammonia water to hot or very acid liquids; incomplete reduction of ferric oxide by not passing hydrogen sulphide for a sufficient time, or the partial oxidation of ferrous oxide by faulty manipulation; the throwing out of a precipitate by incautious application of the jet of water; an improper manner of introducing reagents or precipitants; covering a beaker with the watch-glass *convex-side* up, it must always be convex-side down.

Carelessness.—The errors due to carelessness are the least excusable and are generally the most serious as well as the most easily avoided. They include: injury to the balance or weights by improper handling; placing hot or damp objects on the pan; incorrect replacement of the weights in the box; the spilling of liquids or powders during transfer; the loss of liquids by splashing or "bumping," or of powder by drafts of air or by their "puffing up" on the addition of liquids (p. 100); the use of unclean utensils and of an unclean or untidy work-bench; the dropping or breaking of vessels; the ill-treatment of platinum crucibles, so that they become dented or otherwise injured; laying the stopper of a reagent-bottle on a possibly unclean surface, such as that of the work-bench;[2] the absence of a cover-glass from a beaker during boiling or while standing, or that of the crucible cover during a fusion or ignition; the incorrect labeling or the failure to label the various precipitates and filtrates; not washing used vessels as soon as possible and putting them in their proper place; inattention to the operations in progress; not following closely the directions given.

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[1] This error is especially serious and is one of the faults most often committed by beginners.

[2] A reagent-bottle stopper must never be laid on the work-bench (unless it has a flat top); it should always be held between the fingers or placed in a clean watch-glass.

3. WEIGHING[1]

Preliminary Remarks.—Only a crucible, a glass tube or weighing-bottle, a small watch-glass, a small platinum basin, or the weights should be placed directly on the pan.

The object to be weighed must be perfectly dry, *and must be at the temperature of the room.* Nothing hot, or even slightly warm, is ever to be placed on the balance pans. Apart from the possible injury to the pan, the current of heated air expands the balance arm above it and thus indicates a weight that is greater than the truth. This is only slightly offset by the buoying-up effect of the current. On the other hand, the object should not be colder than the surrounding air, because moisture is liable to condense on it.

No solid reagent of any kind, whether in powder or in lumps, is ever to be placed directly on the pan. All such substances must be placed in and weighed with a receptacle, such as a crucible, watch-glass, or weighing-tube or weighing-bottle.

One balance-pan should be always that on which the object to be weighed is placed. For a right-handed person this would be the left-hand pan, the right-hand pan being reserved for the weights.[1] This rule is to be strictly adhered to, because it eliminates the error due to inequality of the balance-arms (Mellor, p. 22).

When weighing a crucible that weighs, for example, a little more than 19 grams, it is a great temptation, in order to save time and labor, to put the 20-gram weight on the right-hand pan and a 1-gram weight on the left, with the crucible. Although this procedure may be adopted by the experienced analyst, who knows his crucibles, and for the gram weights only, it should be avoided by the student, as it is very likely to cause confusion and error in noting the weights. Above all, it should never be done with the decigram and centigram weights, where the practice is very likely to cause error.

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[1] Fresenius–Cohn, **1**, pp. 21–25; Gooch, pp. 14–24; Hillebrand–Lundell, pp. 12–14; Mellor, pp. 7–27; Treadwell–Hall, **2**, pp. 6–16.

[2] **It is here assumed, as throughout this book, that the chemist is right-handed.**

The object to be weighed, as well as the heavier weights, should be placed at the center of the left- and right-hand pan, respectively. This will prevent the sometimes violent swinging of the pan that occurs when a heavy mass is placed too near its edge; this swinging may be difficult to stop. A weight-burette is to be suspended from the hook above the pan, and a tube is best supported on a light metal frame to prevent rolling.

The pans should not be allowed to have any rotary or swinging motion, because this may injure the knife-edges. If either pan swings on release, the motion should be stopped by gently raising the pan arrest so as to stop the pan at the middle of the swing. On full release, during the observation of the pointer, the pans should hang vertically and with no swinging from side to side.

The weights and crucibles must be handled only with the ivory-tipped forceps, and should be placed on and removed from the pans very gently. Indeed, all motions involved in weighing should be gentle and slow. No weight, not even a centigram one, is to be dropped on the pan.

Both the beam and pans are to be arrested before placing anything on, or removing anything from, the pans. The motion in arrest and release should be very gentle and gradual, and the beam should be arrested only when the pointer is at, or at most not more than one division from, the zero-point. The balance should never ''chatter'' through arresting the beam too quickly. These rules are very important, and neglect of them will inevitably lead to the impairment of the accuracy of the balance.

The balance-case is necessarily opened while putting on the weights needed from the box, but it is to be closed during the weighing with the rider for milligrams and tenths.

The observer should sit directly in front of the center of the balance ''so as to avoid errrors due to parallax in reading the pointer.'' It should be seen that the balance is level and, if necessary, it is to be adjusted to horizontality by the leveling screws and the plumb-bob or spirit-level that should be part of the balance-case equipment. The rider, supported on its hook, should be so far above the beam that there is no possibility of the beam hitting it.

When the beam is free and at rest, and with no load on the pans, the pointer should be at not more than one, or at most two, divisions from the center-point. As Wells[1] points out, much too much attention and importance are given in most textbooks to determinations of the zero-point, and he quotes in full the illustration given by Treadwell–Hall (p. 12) "as a striking example of how weighing should not be done." He advocates the method of short swings, with swings of a maximum of four divisions on either side,[1] and the central point of the scale being taken as the zero-point. This is the procedure that the author has adopted and used for many years, and he never uses the complicated procedure advocated by Treadwell–Hall, Mellor, and others.

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[1] H. L. Wells, Jour. Amer. Chem. Soc., **42**, p. 411, 1920.

If the place of rest of the pointer is more than two divisions from the center-point, the balance should be adjusted so as to bring the point of rest at or within one division of the center-point of the scale by very cautiously moving one of the nuts at the ends of the beam. The balance-beam should be allowed to cool before the final reading (p. 31).

In ordinary analytical work there is no need to use such refinements as correction for the buoyancy of the air, or such accurate but time-consuming methods of weighing as those by Gauss or Borda. The usual method by swings is to be used.

Procedure of Weighing.—The object to be weighed, if it is a crucible, should be ignited at a bright red heat for a few minutes, placed in the desiccator when it has cooled below visible redness (*never when red-hot*), and allowed to cool to room temperature before being weighed. This will take ten minutes or so with a platinum crucible, but much longer with porcelain or vitreosil. The object of the ignition is to drive off adherent moisture and to bring the crucible into the condition in which it will be after the ignition of the precipitate. If the object to be weighed cannot be ignited, but is dried in the oven, it is placed in the desiccator immediately after removal from the oven and allowed to cool to room temperature. A specimen tube, weight-burette, weighing-bottle, or absorption-tube, is to be wiped dry with a clean cloth. Such objects may be handled lightly with the tips of the dry fingers, which will remove any electrification caused by the rubbing.

After having made sure that the pans and beam are arrested, the object to be weighed, say a crucible, is placed on the center of the left-hand pan, and weights approximately equal to that of the crucible[2] on the right-hand pan. The pans are released very gently and if they swing they are to be stopped as described above. Then the beam is very slowly and slightly released, the direction of movement of the pointer is noted, and the beam and pans are again very gently arrested. If the weight on the right-hand pan is too great, the smallest weight is removed, or if it is too small the next larger weight is added; then the pans and beam are released and the pointer observed as before. The process is continued in this way, adding or removing the weights *systematically*,[1] and not at random, until no more weights need be put on the pan, and until 10 milligrams, measured with the rider on the right-hand beam, moves the pointer to the left, in other words, is too much.

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[1] His final swings are of only one-half to two divisions in total length.

[2] It is convenient to have in the balance case a small card on which are written the numbers and weights of the different crucibles in use.

The balance-case is now closed and the weighing is finished with the rider. This should also be carried out systematically; for example, by beginning with the rider at the center of the arm and moving it successively smaller distances. When the weighing gets down to tenths of a milligram (small beam divisions) the extreme excursions of the pointer are to be noted. The tenth-milligram is regarded as final that gives a zero-point the same as that of the empty balance, or when the swings are equal on both sides of the center of the scale if the zero-point is only one or two divisions away.

The beam is swung or set in motion during these final observations by using the rubber bulb or by lightly waving the hand up and down near one pan, *taking care not to touch it.*[2]

Recording the weights in the notebook must be done systematically and uniformly, by first noting down the weights from the vacant spaces in the weight-box, and then checking up as the weights are removed from the pan and replaced in their proper places in the box.

As Fresenius points out[3]: "The student should make it a rule to enter the number to be deducted on the lower line." The entry in the notebook should therefore be in this form:

Cruc. + subst. = 33.0909
Cruc. = 32.0712

1.0197

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[1] The weights should not be placed one on the other, but should be laid down alongside each other and in order from heavier to lighter; this facilitates the checking up of the weights and diminishes the possibility of error in replacing the weights in their proper places in the box.

[2] The beam can also be set in motion by placing the rider on the beam for an instant, or by a "trick" in releasing it; but these should not be tried by the beginner.

[3] Fresenius-Cohn, p. 21.

The uniform adoption of this procedure will lessen the possibility of arithmetical mistakes.

When the weighing is ended it should be seen that the pans are empty and free from dust, the balance case is closed, the rider lifted from the beam, and the weight-box closed, so that all will be safe from dust and immediately ready for another weighing. The practice of leaving weights on the pan, as during the ignition of a precipitate, which is simply to save the slight trouble of taking them off and putting them on again is injudicious. It is one of the small things that mark a person who does not appreciate the fundamental importance of the proper care of a balance.

A word may be said of the practice of so-called "rational" weighing; that is, the weighing out of an exact amount of substance so that the weight of a precipitate will express immediately the percentage of a constituent. Thus, if exactly 0.5303 gram of a substance that contains Na_2O but no K_2O is weighed out, the weight of the NaCl obtained will be the percentage of the Na_2O. This is because the weight of the NaCl is multiplied by 0.5303 to reduce it to Na_2O, and dividing the product by 0.5303 (the weight of substance taken) to get the percentage will, of course, yield a quotient identical with the weight of NaCl.

The only purpose of such weighing is to avoid calculation, and generally laziness here defeats its own object. The mental labor involved in the calculation is very slight, indeed less than that involved in the exact weighing, whereas the latter generally consumes far more time. For both reasons, but especially because of the loss of time, the practice is not commended.[1] The same objection applies to the weighing out of exactly 1.0000 gram of the rock powder.

4. Decomposition [2]

After the portion of rock powder is weighed out it must be decomposed, either by fusion with a flux or by treatment with acid, so as to bring it into solution preliminary to analysis.

Some silicate minerals, such as leucite, nephelite, and olivine, are easily and completely decomposed by hot hydrochloric (or nitric) acid,[1] and the analysis of them (if pure) may be effected after such simple preliminary solution. Others again, such as quartz, orthoclase, and albite, are quite unattacked by acids, while others, such as pyroxenes and hornblendes, are only partially attacked. Since no igneous rock, so far as we know, is composed entirely of the first class of minerals, free from inclusions, and is completely soluble in hydrochloric acid, it is necessary to bring the constituents of the rock into solution by other means, as a preliminary to its analysis.

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[1] Cf. Mellor, p. 54.

[2] A protest is here registered against the phrase "opening up," used by English chemists, instead of "decomposition." The former suggests getting at the contents of a tin of sardines or removing an obstinate oyster from its shell rather than getting a rock or mineral into proper condition for analysis.

A number of reagents and methods have been proposed for this purpose, some of them based on the use of hydrochloric, sulphuric, nitric, or hydrofluoric acids, and others that use various fluxes,[2] as alkali hydroxides, carbonates, or fluorides, calcium carbonate, lead or bismuth oxide, and boric acid. A description and discussion of these is given by the authors cited below,[3] but it is unnecessary to enter into this phase of the matter here. It will suffice to describe those methods of decomposition that recommend themselves to the author and to the chemists of the U. S. Geological Survey and of the Geophysical Laboratory.

In order to determine the different constituents of a rock, different reagents and methods of decomposition are found to be appropriate, depending on the different constituents to be determined in a given portion of the rock powder. The chief ones are:

1. Fusion of the rock powder with sodium carbonate, for all the major constituents (except ferrous oxide and the alkalies), and also for zirconia, baria, sulphur, etc.
2. Fusion of the ignited ammonia precipitate with potassium pyrosulphate, for total iron oxides and titania.
3. Ignition of the rock with calcium carbonate and ammonium chloride, for the alkalies.
4. Solution of the rock in a mixture of sulphuric and hydrofluoric acids, for ferrous oxide and for manganous oxide.

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[1] Such soluble minerals themselves almost always contain insoluble inclusions. This may be the reason for the experience of Duparc (Bull. Soc. Franç. Min., **42,** p. 148, 1919), who found that a small portion of olivine resists strongly the attack by acid. A flux, such as sodium carbonate, is to be used, instead of hydrochloric acid, to decompose such "soluble" minerals.

[2] Hillebrand–Lundell (pp. 698–703, 706–707) give a very good discussion of the various fluxes and their choice.

[3] Chesneau, pp. 294–302; Dittrich, p. 4; L. Duparc, Bull. Soc. Franç. Min., **42,** p. 151; Fresenius–Cohn, **1,** pp. 511–521; Hillebrand, Bull. **700,** pp. 89–97; Hillebrand–Lundell, pp. 698–713; Jannasch, pp. 298–352; Mellor, pp. 160–166; Treadwell–Hall, pp. 415–420. The discussion in Hillebrand–Lundell is particularly useful.

5. Solution of the rock in a mixture of nitric and hydrofluoric acids, for phosphorus pentoxide.

6. Digestion of the rock with dilute hydrochloric acid, for sulphur trioxide.

7. Digestion of the rock with dilute nitric acid, for chlorine.

The methods employed, and consequently the procedures, are so different that few general rules can be laid down, and the special precautions to be observed in each case will be described in its proper place later. A few general suggestions as to procedure are given here.

In adding any flux to a rock powder care should be taken that none of the powder flies up and is lost.

The rock powder and the flux should be well mixed, and the platinum spatula used for this should be carefully cleaned by rubbing with a little extra flux, which is added to that in the crucible.

The mixing of calcium carbonate and ammonium chloride with the rock powder must be so intimate that it demands special treatment, as described on page 224.

The heating of a mixture of flux with the rock powder should begin at a low temperature and the heat gradually raised to the maximum desired.

Care should be taken to see that there is no spattering of the molten liquid and in the pyrosulphate fusion, especially, there is need of a very gradual increase in temperature.

Blasting of ignited precipitates is seldom called for, and is to be avoided if possible.

In dissolving rock powders in acids, two points are to be specially attended to. The first is the liability of fine powders to fly off when mixed with liquid. This can be avoided by carefully dropping in a very little water, in order to moisten the powder, before adding the acid. The tip of the wash-bottle should be full of water so as to cause no puff of air, and it should be inserted beneath the slightly raised crucible cover, which is lowered into place immediately. The second point is that here, also, there should be no spattering, so that the heating must be cautious and gradual at first, and the liquid must never boil or bubble.

Evaporations and digestions in which vapors of strong acids are given off,[1] should be conducted under the hood, which should have an efficient draft. This is necessary, not only on account of the comfort and health of the analyst, but also to prevent contamination of the laboratory atmosphere. Operations that are to be carried out under the hood include: the evaporation of hydrochloric acid to render silica insoluble in the main portion (p. 157); the digestion with sulphuric and hydrofluoric acids for the determination of manganous oxide (p. 251), and with nitric and hydrofluoric acids for that of phosphorus pentoxide, and the reduction of iron by hydrogen sulphide (p. 184).

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[1] The solution of the rock powder in sulphuric and hydrofluoric acids for FeO, and the fusion with pyrosulphate, may be conducted outside the hood.

5. PRECIPITATION[1]

The precipitant must be capable of precipitating quantitatively the substance to be determined; must not introduce any substance that may interfere with subsequent precipitations in the filtrate; and any excess of precipitant must be readily removable from the precipitate by washing.

The ideal precipitate must be insoluble in the liquid in which it is formed; must be wholly precipitated and as quickly as possible; must not inclose any of the mother-liquor, and should not adsorb any of the substances present in the solution; must be in such form as not to pass through the filter, and be readily and completely washed free from impurities; and, finally, must be capable of being changed on drying or ignition to a definite and stable substance of known and invariable composition.

It is seldom, if ever, that we can attain all these optimal desiderata, and we must rest content with reducing the sources of error to a minimum. The following rules will be found generally applicable, but precipitates vary so much in character that some will demand special modifications of treatment.

The solution to be precipitated should seldom be highly concentrated, as the precipitate will then be more apt to adsorb and carry down substances present in the solution, and any mother-liquor retained by it will constitute a relatively great impurity. On the other hand, it should not be very dilute, partly because no precipitate is absolutely insoluble, partly because more time will be needed for complete precipitation, and partly because it will add to the volume of the liquid to be filtered.

The precipitant is not to be added all at once, but slowly, as this tends to the formation of not only a coarser and more easily washed precipitate, but one less contaminated with adsorbed substances. Furthermore, coarse-grained precipitates are less soluble than are fine-grained ones.[1]

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[1] Blasdale, pp. 115–145; Farnsworth, pp. 42–53; Fresenius–Cohn, 1, pp. 91–92; Gooch, pp. 57–62; Hillebrand–Lundell, pp. 68–74; Mellor, pp. 95–97; Ostwald, p. 75; Stieglitz, pp. 122–138, 145–155.

The precipitant should not be added in such a way as to splash; and if the addition is likely to cause bubbling or effervescence the beaker should be covered with a watch-glass, and the liquid is to be added through a funnel with bent stem.

The solution should be well stirred during the addition of the precipitant, and for a minute or so after, to ensure a thorough mixture. The stirring-rod should be so long as to be handled in the subsequent filtration without the fingers coming into contact with the precipitate or the liquid adhering to the rod; it should project about 5 to 7 cm. above the final bulk of liquid and, of course, should extend above the beaker rim. The stirring-rod should never be placed in the lip during the precipitation and washing.

A decided, but not extravagant, excess of the precipitant must be added to ensure complete precipitation. This is because of the diminution in solubility of a salt in solution in the presence of an ion common with it. The addition of the theoretically exact amount of precipitant necessary never produces complete precipitation, and the excess may be defined as the extra amount needed to bring this about.[2]

No general rule can be laid down as to what this excess may be; but the beginner should avoid adding inordinate amounts of precipitant. To make sure that one has added a sufficient amount, until, and in most cases even if, one has had experience, it is well after allowing the precipitate to settle, to add a few drops or cubic centimeters of the precipitant and observe whether, after a short time, there is further precipitation. In some cases considerable time must be allowed for this, and then the test may be carried out in the first few cubic centimeters of the filtrate, this being returned to the main portion if a precipitate forms, and more precipitant is to be added to the whole. The test may also be made by pouring a little of the precipitant into the beaker in which the filtrate is received.

Many precipitates are so fine-grained, or even ''amorphous'' or colloidal when first formed, that they pass through the filter. This is prevented by allowing the precipitate to stand for some hours in the liquid in which it has been formed, before filtering. In this way the larger crystals grow at the expense of the smaller, and the whole mass of the precipitate becomes more coarsely crystalline.[1] This is facilitated by standing in a warm place. Some precipitates, such as ammonium magnesium phosphate, form slowly and, with these, it is necessary to let them stand for some hours or even over-night for complete precipitation. It is often advantageous, as with calcium oxalate, to precipitate in a hot, or even a boiling, solution, as this procedure renders the precipitate more coarsely crystalline and less liable to run through the filter paper.

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[1] Cf. Stieglitz, p. 123.

[2] Cf. Gooch, p. 5; Mellor, p. 182, note 9; Ostwald, p. 80.

In some cases it is well to add to the solution before precipitation a liquid in which the precipitate is but slightly soluble.[2] This not only renders the precipitate more coarsely crystalline, but lessens the time needed for complete precipitation. For this reason alcohol may be added in the precipitation of calcium and magnesium, and ammonia also in that of the latter.

Gelatinous precipitates, such as aluminum hydroxide and ferric hydroxide, are not only very difficult to wash free from adsorbed salts, but they tend to form colloidal solutions, and pass through the filter. This can be prevented by the presence of electrolytes in the solution, such as easily soluble and crystallizable salts.[3] Ammonium salts, especially the chloride and nitrate, are generally used for this purpose, as they are driven off on ignition.

Such gelatinous substances should always be precipitated in hot liquids. After precipitation the liquid may be brought to boiling as this effects coagulation. The boiling should not be long continued, as this tends to make the precipitate slimy and difficult to filter and wash. Liquids that contain gelatinous precipitates are very liable to "bump," which may easily lead to loss. They should, on this account, be watched and stirred during the heating.

Because of the impurities present in almost all precipitates, and especially in gelatinous ones, through adsorption,[4] coprecipitation, or inclusion of the mother-liquor, which cannot be removed by washing, it is always advisable, and is necessary for good work, to redissolve the precipitate (after slight washing), and to reprecipitate after dilution. If the reprecipitation is effected by neutralization of the acid solution, a small quantity of the original precipitant is previously added to insure the presence of an excess of a common ion.

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[1] Blasdale, p., 117; Fresenius–Cohn, **1**, p. 92; Gooch, p. 58; Mellor, p. 96; Ostwald, p. 22.

[2] Blasdale, p. 124; Gooch, p. 58; Mellor, p. 96; Ostwald, p. 22.

[3] Cf. Blasdale, pp. 56, 124; Gooch, p. 60; Mellor, p. 95; Ostwald, p. 24; Stieglitz, **1**, pp. 125–138.

[4] Cf. Blasdale, p. 136; Gooch, p. 61; Mellor, p. 96; Ostwald, pp. 18, 84.

Before filtration, the precipitate is allowed to stand until the solution above it is clear, or until one is certain that the precipitation is complete.

Very small amounts of white precipitates may escape notice. They may be detected by gently stirring the liquid, when the precipitate collects in a small heap at the center of the bottom of the beaker.

6. Filtration and Washing[1]

The filtration needed in the analysis of rocks is of two kinds; simple filtration, in which a filter paper is used and where the filtrate passes through by its own weight and at practically atmospheric pressure; and suction filtration, in which either filter paper or some other filtering medium, such as asbestos, is used, and the process takes place under diminished pressure, so that the filtrate is sucked through the filter. Each method has its advantages and is specially suited to different precipitates and conditions.

Simple Filtration.—This method is that most generally used, and is the one best adapted to precipitates that can be ignited with the filter paper without change in composition, and especially to cases where the filtrate is to be used for subsequent precipitations.

The funnels and filter papers have been described (pp. 41, 52), and the first requisite is to select the appropriate sizes of filter and funnel. It is a common fault of beginners to use too large a filter, and this is, as Treadwell says: ''One of the inexcusable analytical errors.''

A filter paper is to be selected that is as small as possible, so as to diminish the amount of washing needed, and yet that will contain all the precipitate and a sufficient amount of wash-water; on the other hand, it must not be too small. If the precipitate is very large or bulky it may be advisable or necessary to filter through two filters in separate funnels, but this should seldom happen. The size will, of course, differ with different precipitates, and appropriate sizes are mentioned later in the course of the descriptions of the different methods.

Two principles are, however, to be borne in mind. The first is that the size of the filter should be regulated rather by the amount of the precipitate than by the volume of the liquid to be filtered. This principle must, however, be modified in cases of large volume of liquid and small amounts of precipitate, as frequently happens in the determination of lime and magnesia.

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[1] Blasdale, pp. 146–155; pp. 54–60; Farnsworth, pp. 54–60; Fresenius–Cohn, **1**, 94–109; Gooch, pp. 62–67; Hillebrand–Lundell, pp. 89–96; Ostwald, pp. 13–15; Treadwell–Hall, pp. 25–32.

The second principle is that, although the filter should be as small as possible, it should be more than large enough to contain all of the precipitate, and that the whole precipitate should not occupy more than one-half, or preferably about one-third, of its volume. The moist precipitate should not reach up to less than about 3 mm. of the edge of the paper.[1] It must never rise above it, or soil the glass of the funnel, which should be neither too small nor too large for the filter. When folded and put in place the edge of the filter should be about 1 cm. from the rim of the funnel.[2] The filter must never reach to the funnel's rim, or project beyond it. Appropriate sizes of filter and funnel are as follows:[3]

Diameters, in centimeters

Filter[3]	5½	7	9	11	12½
Funnel	3½	4-5	5-6½	6½-7½	7½-9

In general, the 9-cm. filter and 6½-cm. funnel are those most often used, and the 11-, 7-, and 5½-cm. filters, and 5-, and 3½-cm. funnels respectively are less often needed.

The paper filter may be folded in two ways. The form almost always used is as follows:

The dry filter is first folded exactly in half, and then again in half (from the center-point of the diameter), so as to form a quadrant. The folds are lightly pressed down with the finger tips beginning a few millimeters from the tip so as to leave this unpressed, as it might otherwise break. The dry filter is then opened out, placed in the funnel, and fitted snugly into place. If the walls of the funnel are straight and the apical angle is exactly 60° the filter folded as described above will fit snugly into the funnel without further folding. If, however, the angle is not exactly 60°, the paper at the second fold-

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[1] The ammonia precipitate (p. 170) is an exception, as this is so bulky that it is often necessary to let it rise closer to the edge of the paper. The same is true of some of the precipitates formed by organic reagents, such as cupferron.

[2] See frontispiece.

[3] It may be convenient to know the volumes of the cones, (apical angle = 60°), formed by filter papers of different sizes. They are (approximately) as follows:

Diameter (cm.)...........	5½	7	9	11	12½
Volume (c.c.)...........	2.0	3.3	5.5	8.2	10.6

ing is to be folded from the center of the diameter, into slightly more than a quadrant; and is then opened out on the larger or smaller side according as the funnel angle is greater or less than 60°. A funnel had best be rejected for analytical work if its angle is decidedly greater or less than 60° or, without question, if its walls are not straight.

A second method of folding the filter, which permits much more rapid filtration and in some cases may replace the use of the filter-pump is as follows:[1]

The dry filter is first folded exactly in half, as above, and, after being opened up is folded again at right angles to the first fold and on the same side. The paper is next turned over and folded at an angle of about 30° with the first, and again at right angles to this. The paper is then fitted into the funnel, with the small gores outward and overlapping in the same direction. It is important that the creases should not be too sharp, especially near the apex, because this weakens the paper.

When, having used either of the two methods of folding, the filter is in place in the funnel, it is held down with a finger tip and is wet slightly all over with a jet of water from the wash-bottle. Any excess of water is allowed to drain through the stem, and *is not poured out,* as this may later cause "creeping" of fine precipitates up the wet glass. With a finger tip the filter is now pressed gently against the glass. Care should be taken to press out any air bubbles, and to press down the creases made by the folds, along their lengths and especially at the rim of the filter, because they are liable to form air channels and retard filtration or lead to loss of precipitate if the filter is, by mischance, overfilled. All this should be done gently and without any rubbing motion, or the tender, moist paper may be torn. If this happens the torn paper is to be rejected and a new filter prepared.

The funnel is then placed in the funnel stand, care being taken that the tip of the stem does not touch the wood in passing. Beneath is placed a beaker of the size suitable to hold the filtrate, as will be suggested in the descriptions of the different determinations. The beaker should be clean, even if the filtrate is to be rejected, and it is best to rinse it out first with a little water from the wash-bottle. If any precipitate passes through it may thus be recovered. The tip of the funnel stem should be close to, but not touching, the side of the beaker, and be within about 5 cm. of the bottom, to prevent spattering. As the filtrate accumulates in the beaker the arm of the funnel stand is to be raised to keep the tip about the same height above the surface of the liquid. The tip of the funnel should never be allowed to dip into the liquid.

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[1] The author is indebted to Mr. D. D. Schurtz for making him acquainted with this method of folding. A somewhat similar method of folding is described by Hillebrand–Lundell, p. 90.

The beaker containing the liquid and precipitate to be filtered is allowed to stand until the precipitate settles and the liquid above is perfectly clear, which will usually be the case during the preparation of the filter paper in the funnel. The beaker is then taken in the right hand[1] and held above the funnel, the stirring-rod (held in the left hand) rested vertically against the lip of the beaker, projecting about 5 cm. below this. The beaker is then tilted gently until the liquid flows slowly down the rod[2] and into the filter. The stream is to be directed against the side, not the tip, of the filter, and this should be filled only to within about 3 mm. of the rim, so that the edge is kept quite free from precipitate. The liquid must never be allowed to overflow the filter.

However clear the upper liquid may appear, or however large its volume, it must never be decanted directly into the other beaker, but *must always be passed through the filter.* Particles of precipitate float on the surface or in the mass of liquid and may escape notice and be lost, unless they are caught on the filter. This applies to even the heaviest precipitates, such as silver chloride, so that the simple decantation as recommended by Fresenius (p. 93), and Farnsworth (p. 58) without filtration, must not be used.

If the filter has been properly fitted and the funnel and suction tube are clean, the tube will fill with a column of liquid that causes a gentle suction. Generally, after the column is established the liquid will flow through in a steady stream for the first few minutes. During this time the beaker and rod are to be kept steadily in place above the filter, the tilt of the beaker being gradually increased to maintain the level of the liquid in the filter. There must be no "slopping," and as little of the precipitate as possible should enter the filter.

After a time the filtrate begins to pass slowly and to issue from the stem in drops, because of the gradual clogging of the paper by the precipitate. The beaker may then be replaced on the work-bench from time to time (to rest the hand), and the stirring-rod placed in it, but without stirring up the precipitate. The rod should not be placed in the lip. As has been said already, the rod should be long enough to permit handling without touching the adherent precipitate with the fingers. The liquid should be thus poured into the filter from time to time, as it empties, not allowing the filter to empty so far as to break the column in the suction-tube. If an air-channel develops beneath one of the creases, allowing bubbles to pass into the tube, the open upper ends are to be gently pressed down and closed with the tip of the stirring-rod, without breaking the paper.

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[1] Here and elsewhere it is assumed that the operator is right-handed.

[2] The liquid must never be poured directly from the beaker into the filter without the aid of a rod, as it is apt to drip or splash.

As more and more of the liquid passes into the filter the last portion left in the beaker becomes quite thick with the precipitate.[1] If the precipitate is to be redissolved, as will almost always be the case, most of the precipitate should not be allowed to pass into the filter. The sides of the beaker are to be washed down with a little water, directed from the tip of the wash-bottle all around, from the upper level of the adherent precipitate down. After standing a few minutes and allowing the precipitate to settle, the liquid is poured into the filter as before, as little as possible of the precipitate going with it. This washing is repeated only three or four times. The beaker with the precipitate is then substituted for that with the filtrate, the exchange being made so that no drops are lost.

A sufficient amount of the appropriate solvent (generally a dilute acid) is prepared in a small 100-c.c. beaker, and the filter is filled nearly to the top with this. As it dissolves the precipitate in the filter and passes through the Piccard tube,[2] it is allowed to drop against the side of the beaker below, above the upper line of adherent precipitate. The beaker is held somewhat slanting and close to the tip of the stem so that the drops do not bounce off. As the solvent drops, the beaker is turned around until all the precipitate covering its interior is acted on and dissolved.

When the filter is empty it is again filled with the solvent, and, if necessary, the solution of adherent precipitate is completed, while the stirring-rod is cleaned of precipitate by some drops of solvent running down it. After several repetitions, by which time all the precipitate in the filter should be dissolved, and during which the beaker below is placed upright on the base of the stand and the funnel is lowered to prevent splashing, not more than about 50 c.c. of solvent should have been used.

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[1] The description here applies to ordinary, crystalline precipitates such as those of calcium oxalate and magnesium phosphate. Gelatinous ones need somewhat different treatment, as will be described under "Ammonia Precipitate" (p. 170).

[2] A turbidity appearing in the Piccard tube is but momentary and need cause no concern. It is due to neutralization of the acid by the ammonia remaining in the tube causing reprecipitation.

The filter is then washed four or five times, the liquid passing, of course, into the beaker below, and the sides of the beaker and the stirring-rod are washed down. This should all be done so that not more than 100 or 150 c.c. of liquid and washings containing the dissolved precipitate are in the original beaker.

The liquid is then warmed, a few drops of the precipitant are added and reprecipitation is brought about by the addition of the proper reagent. During this operation the contents of the beaker are to be stirred constantly. The beaker (covered and labeled) is set aside for some time to insure settling and complete precipitation.

If the precipitate is not to be reprecipitated (or after the last reprecipitation) all of the loose precipitate, after standing, is brought into the filter with the liquid. The sides of the beaker, from above the line of adherent precipitate, are washed down once or twice and after each washing the contents of the beaker are poured into the filter, which is each time allowed to empty. In what follows the filter is allowed to drain after each addition.

The beaker is then taken in the left hand, held tilted slightly down (mouth to the right) and the lip down and above the filter. The rod is placed across the beaker, resting in the lip and the tip projecting a few centimeters, the upper half held firmly in place with the left forefinger. The interior is then washed with a jet of water, commencing on the now upper side, and sweeping the precipitate down. Small portions of water are to be used at a time, and all the loose precipitate is to be washed into the filter.

The beaker being set down, its walls and the rod are well wet with water, and the precipitate adherent to them is rubbed loose with a ''policeman'' or rubber-tipped rod. This should be done systematically and thoroughly.

The rod is attended to first; held above the beaker, the portion with adherent precipitate is rubbed along its whole length, the rod being turned so that the entire surface is treated, the tip not being neglected. It is then washed off with a little jet of water into the beaker, examined to see that it is free from precipitate, and laid across the funnel.

The interior of the beaker is then rubbed clean, also systematically. This may best be done by rubbing a sector of a few centimeters wide at a time, rubbing sidewise from top to bottom; then another adjacent sector, and so on. The rubber is occasionally wet with the liquid in the bottom of the beaker. The bottom is finally rubbed clean, best by beginning with complete circular sweeps around the bend, and gradually working in to the center. The precipitate on the rubber is washed into the beaker.

All of the now loose precipitate is then washed into the filter, as just described. The interior of the beaker is examined in a good light, and any adhering patches of precipitate are to be rubbed off and washed into the filter, until the beaker and rod are entirely clean and all of the precipitate has been brought into the filter.

The whole amount of precipitate should not more than half fill the filter, and should not reach to above 5 mm. of its edge. It is best that the mass of precipitate does not have a flat surface but be rather thicker and lower toward the apex and thinning out at the sides.[1]

Washing of Precipitates.[2]—The precipitate has now to be washed, and in doing this one has to steer between the Scylla of not washing it free from all contaminating salts, and the Charybdis of over-washing and thereby dissolving some of it. It is, therefore, most desirable not to wash beyond the point at which the impurities in the wash liquid and adherent to the precipitate are just entirely removed or are reduced to unweighable (and therefore negligible) amount. This will also have the advantage of keeping the bulk of filtrate at a minimum. The theory of the matter is discussed in sufficient detail by the authors cited above so that it need not be gone into here.

The general principle to which the discussion leads, one that should be borne in mind and applied to all washings, is that the washing is more efficient and therefore less wash liquid is needed if it is done with *many small portions* than with a few large portions of equal total volume. In the washing, therefore, the precipitate should be little more than covered with water and allowed to drain each time.

No generally applicable rule can be given as to the total amount of wash liquid (for example, water) that should be used for proper washing. One should achieve the ideal of using sufficient wash-water to remove the soluble salts completely and also not using too much, so that the precipitate is dissolved to an appreciable extent. Four (certainly five or six) washings should, theoretically, practically free the precipitate from soluble salts, as is explained in the references cited above. But this is seldom actually true, so that most, if not all, precipitates should be washed many more times, up to ten or so, before the washing can be considered as complete. This is especially true of gelatinous precipitates.

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[1] Cf. Treadwell–Hall, Fig. 5, p. 27.

[2] Blasdale, pp. 151–153; Fresenius–Cohn, **1**, pp. 98–100; Gooch, pp. 62–63; Hillebrand–Lundell, pp. 94–96; Ostwald, pp. 15–22; Treadwell-Hall, pp. 25–29.

The tendency of beginners is both to use too large portions of the wash-water, and to over-wash the precipitate, though there are exceptions when impatience leads to under-washing.

In washing precipitates, several practical precautions are to be observed. The jet of water is first directed against the edge of the filter, and carried two or three times around the upper zone that is free from precipitate. This will clear the portion of soluble salts.

The first impact of the jet should never be directed against the precipitate, as some of the precipitate is very liable to be thrown out and lost. It should therefore be aimed first at a clean space of the filter and from this gently directed against the edge of the precipitate.

After washing the rim clean, the precipitate is gradually worked downward with the jet, *letting the filter empty* after it becomes about half full. When all of it has been collected at the bottom of the filter, the mass of precipitate should be well mixed with water several times, great care being taken that none of it is thrown out by a too violent application of the jet, and that not too much water is used. Each time some of the precipitate will be again spread above the main portion, but at the end of the washing the precipitate should all be collected at the bottom of the filter, with the upper sides clean. A little practice will enable one to do this easily.

The filter should not be filled with the wash liquid, especially if the precipitate tends to creep; and, above all, the filter must not be allowed to overflow. The narrow zone along the edge is to be kept free from precipitate as far as possible, and attention should be paid to washing all soluble salts out of it. The funnel should drain well after each addition of wash liquid, especially during the last stages. It is advisable, if possible, to have a common ion in the wash liquid, to reduce the solubility of the precipitate. This is most needed, indeed necessary, with colloidal precipitates, as will be explained when describing the ammonia precipitation (p. 17).

After (not before) the precipitate has been mixed with water eight or ten times, one should test the filtrate for a soluble salt, usually chloride or sulphate, which will indicate whether the washing is complete or not. For this, the tip of the suction tube is washed off with a small jet of water, as previous portions of the filtrate are apt to creep up the outside and thus show impurity when the actual liquid in the filter is free from it. A little more water is added to the precipitate, the funnel is raised after the column of liquid in the tube has been driven out, and a few drops of the uncontaminated filtrate are caught on a small, clean watch-glass. These are then tested with the appropriate reagent, silver nitrate for chlorides, after the addition of a drop of nitric acid, or barium chloride for sulphates. By this time the drops should contain so negligible an amount of dissolved salts that they may be rejected. This testing is to be repeated after each three or four washings, until there is no reaction. The precipitate is now ready for drying and ignition (p. 117).

Suction Filtration.—This method has the advantage of greatly shortening the time necessary for filtration, but is not well adapted to cases where the filtrate is to be used later. The Gooch modification, however, is especially useful, indeed now quite indispensable if the precipitate undergoes change on ignition with filter paper, or if it can not be ignited and must be dried at a low temperature.

The simplest form, in which the filter is of paper and supported in the funnel by a perforated platinum cone, to prevent rupture under pressure, is so seldom used in the analysis of rocks that little need be said of it here.

A funnel with ordinary stem is used, this fitting tightly a single-perforated rubber stopper that closes a filtering flask with stout walls. If it is desired to use the filtrate later, this flask must be well cleaned, but it is better to use Witt's filtering apparatus, with the stem of the funnel projecting into an Erlenmeyer flask instead of a beaker.

The perforated platinum cone, best seamless, should fit the funnel accurately. Especial care should be taken in fitting the paper closely against both the metal and the glass, which may be done by folding the paper the second time into very slightly (1°-2°) more than a quadrant. If it is not properly fitted it will almost surely be torn at the junction.

The suction should be applied gently and increased gradually, and the final pressure should not be too great; only experience can teach what this should be. The filtration and washing are conducted as in the simple method, except that the funnel may be emptied more frequently, though in the washing the precipitate should be well stirred with water to guard against the formation of channels.

Gooch Crucible.[1]—In the Gooch method the filter consists of a layer of asbestos on the perforated bottom of the crucible, the filtration being effected by rather strong suction. The crucible may be of either platinum, fused silica, or porcelain, but the first is preferable, as it is heated and cooled more quickly. An appropriate size has been mentioned on p. 38. As an example of the usual practice, the filtration of ammonium-magnesium phosphate may be taken; that of potassium chloroplatinate demands some slight modifications in detail, which will be noted in the proper place (p. 233).

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[1] The weight of Gooch asbestos crucibles has been found to be very constant. Cf. J. I. Phinney, Am. Jour. Sci., **45**, p. 468, 1893.

A band of soft, thin, black gum tubing about 3 cm. long is slipped over the wide end of the filter tube which it should fit closely for about 1 cm., the other two-thirds extending vertically above the rim. The crucible is put into place in this so that it fits snugly. The filter-tube is inserted in the closely-fitting rubber stopper which is fitted tightly into the filtering-flask, and this is connected with the suction.

A little of the well-shaken asbestos suspension is poured in, about 2 or 3 c.c., but experience must teach one the right amount. The felt when ignited should not be more than about 1 or 2 mm. thick, and may weigh about 5 to 10 centigrams. The suction is turned on and the crucible is gently emptied. It is filled with water five or six times, the jet being directed against the side to avoid tearing the felt. It is thus washed until no asbestos fibres come through, 50 to 100 c.c. of water being ample,[1] and it is finally sucked dry under somewhat increased pressure.

It is sometimes advisable to use a thin, circular, perforated disk of porcelain, which is placed on a thin layer of wet asbestos first applied and sucked, and the disk covered with an upper layer of asbestos. Otherwise the filter is prepared as above. Though the disk somewhat retards the filtration, it protects the felt and decreases the liability of its being torn. If due care is used, however. the use of a disk is found to be unnecessary.

The crucible is heated over a low flame, the bottom cap being left off, and the flame moved about by hand. In this way the felt is well dried without loosening or blistering, as the steam generated from its lower side will escape through the perforations. When quite dry, as is indicated by the whiteness of the asbestos, the bottom cap is put on, and the crucible is covered and ignited at a bright-red heat for a short time, to drive off all traces of water.[2] It is then cooled in the desiccator and weighed.

The Gooch crucible, with the bottom cap and cover removed, is placed in position in the carbon filter, care being taken when inserting it in the rubber mouth, that the latter does not come in contact with the bottom of the crucible and rub off any small pieces of asbestos which may project beyond the perforations. In order to prevent loosening the felt by the upward pressure of the air in the flask, the suction should be turned on before inserting the crucible in the filter tube.

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[1] The author believes that the large volumes recommended by Mellor (p. 105) are not necessary or advisable.

[2] If there is no bottom cap, or the crucible is of porcelain, it is placed within another, larger, platinum crucible for ignition.

The suction should be gentle and at the same time effective. The liquid is poured slowly into the crucible, the stream from the stirring-rod striking the side and not directly on the felt. Otherwise the latter is liable to be torn and some of the perforations laid bare, possibly allowing some of the fine precipitate or asbestos to pass through. The whole of the liquid is thus filtered, with some of the precipitate entering the crucible, so as to protect the felt. The beaker is then rinsed with a stream of (in this case) very dilute ammonia water several times, the bulk of the precipitate going into the Gooch crucible. The adhering precipitate is loosened from the sides and bottom of the beaker and from the stirring-rod by means of a rubber-tipped rod, as already described, and the last traces of it are brought into the filter by gentle streams of the dilute ammonia from the wash-bottle.

The precipitate on the felt is well washed with the same fluid, the stream being directed against the side of the crucible, not on the felt. The crucible is allowed to empty before each addition, of which about half a dozen will be sufficient in most cases. If desired, the washing can be tested by stopping the suction, removing the stopper of the Erlenmeyer flask, and letting a few drops fall on a watch-glass. These are acidified with a drop or two of nitric acid and tested with silver nitrate. It will be well to do this the first few times, till one learns by experience when the precipitate is thoroughly washed.

When the washing is complete, the suction is continued for a short time, in order to partially dry the precipitate, the connection is shut off, and the stopper is cautiously loosened, so as to prevent regurgitation of any liquid that may remain in the tube, up against the felt. The bottom cap, if there be one, is put on, and the crucible is ready for ignition (p. 120).

Munroe Crucible.—The use of metal felt instead of asbestos for filtrations was first suggested by C. E. Munroe in 1888,[1] who proposed especially the use of platinum.

This substance has many advantages over asbestos, among them being the difficulty of obtaining the latter of the proper quality, the rapid filtration if the platinum felt is properly prepared, and the possibility of dissolving the precipitate from the crucible without injury to the felt, for use again.

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[1] C. E. Munroe, Jour. Anal. Chem., **2**, p. 241, 1888; W. O. Snelling, Jour. Am. Chem. Soc., **31**, p. 456, 1909.

A unique practice introduced by Munroe was, in repeated determinations of the same constituent by the same method, to retain the residues on the filter, and use the final weight of one determination as the initial weight of the next, thus saving the time and labor of one weighing operation. This is feasible only when the residue on the filter is permanent, as exposed in the desiccator or balance case, and also when this residue is not dissolved or acted upon by the filtrates and wash water to which it is exposed in subsequent operations. By this means a saving of time, labor, and money is effected.

The descriptions that follow are based on the descriptions by Munroe and by Snelling. A concentrated[1] solution of chloroplatinic acid is precipitated by ammonium chloride in slight excess. The resulting precipitate of ammonium chloroplatinate is washed several times with water and finally with alcohol, the excess of alcohol being poured off as soon as the ammonium chloroplatinate has settled. A perforated platinum crucible[2] (one preferably in which the perforations are numerous and small) is then placed on several layers of filter paper (or a square of clean, white blotting-paper), and held firmly in this position while the alcohol-moist mass of ammonium chloroplatinate is poured into it, usually to a height of from 0.25 to 0.50 cm. The alcohol will be rapidly absorbed by the filter paper upon which the crucible is pressed, and at the expiration of a few moments the surface of the salt will show that all of the excess has been taken up by the paper, the crucible being held firmly against the absorbent paper until this occurs. The moment at which the last of the excess alcohol is absorbed is readily noted by the sudden ''drying'' of the surface of the chloroplatinate.

The crucible can now be removed from the filter paper, and if the operations have been properly performed, an even layer of ammonium chloroplatinate will be found to cover the bottom of the crucible. The crucible is now dried in an oven at about 110° C. until the alcohol is entirely driven off, and then, after the cap and cover have been put on, it is slowly and cautiously heated (over a rather low flame) until the ammonium chloroplatinate is entirely decomposed, the heating being gradually increased and continued, at a dull red heat, and then allowed to cool slowly.

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[1] The stock solution, containing either 0.05 or 0.10 gram of platinum per cubic centimeter may be used. The amount should be sufficient to make a felt weighing from 0.05 to 1.0 gram. The felt in use in my laboratory weighs about 0.8 gram.

[2] Cf. p. 38.

The layer of coherent platinum sponge that covers the bottom of the crucible is sometimes continuous but more often cracked. The felt, in either case, is lightly pressed down and slightly burnished with a glass rod flattened at the end, special care being taken to spread from the center toward the edges, as the felt, on heating, contracts and draws away from the sides. The pressure, however, must not be so great as to interfere with the porosity. If there are cracks they disappear during the burnishing, but it is best to patch them by adding a few drops of chloroplatinic acid solution to the felt and to reheat, at first gently and finally to redness. The final surface should be continuous, smooth, and light silvery-gray. If the final result is not successful the felt may be removed with the platinum spatula, (and added to the bottle of ''platinum residues''), and the whole operation must be repeated.

The felt is remarkably porous, although capable of retaining the finest precipitates, and filters very rapidly—when properly prepared much more rapidly than the asbestos felt. If it is used exclusively for the collection of potassium chloroplatinate in the determination of potash (as is the practice in the author's laboratory) the salt (weighed) is left in the crucible, which is used for the next filtration; the successive amounts of potassium chloroplatinate gradually increasing in weight. If this is done the covered crucible should be placed, after weighing, in the balance case; this will ensure constant weight.

If the Munroe crucible is to be used for other filtrations (such as those of calcium oxalate or magnesium ammonium phosphate),[1] these may be removed by appropriate solvents, a list of which is given by Swett.[2]

A circular piece of fine platinum wire gauze of suitable diameter laid on the bottom of the crucible before pouring in the ammonium chloroplatinate renders the felt tougher and less liable to injury, but it is not necessary.

Filtration with the Munroe crucible is carried out as with the asbestos crucible.

Sintered-glass Filter Crucibles.—Filter crucibles of vitreosil

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[1] It must never be used for the filtration of the ammonia precipitate, at least in rock-analysis.

[2] O. D. Swett, Jour. Am. Chem. Soc., **31**, p. 928, 1909.

(fused silica), with a filter of sintered fused silica powder, may also be used. Filtration is done as with the Gooch or Munroe crucibles, but less precautions may be taken to prevent injury to the filter. These crucibles may be heated to high temperatures and they do not crack on cooling. The Jena glass filtering-crucible, with the filter of sintered glass powder, is of the same type, indeed the original form. These should not be heated above about 250° C., and must be cooled *very slowly*, or they will crack. Either of these crucibles may be freed from the precipitate by solvents, as described by Swett in the paper cited above.

7. Drying and Ignition of Precipitates.[1]

When the precipitate has been filtered and washed, it has to be dried and brought into a condition of stable and definite composition for weighing. The method to be adopted for this purpose depends on whether or not the precipitate is changed on heating with filter paper.

Drying.—If it is a matter of drying at a low temperature, such as with the rock powder for hygroscopic water, or potassium chloroplatinate, the substance, contained in an ordinary platinum or a Gooch crucible, according to circumstance, is dried in the hot-air oven.

Weighed filter papers must never be used, because of the hygroscopicity of paper. The Gooch crucible has entirely supplanted, or at least should entirely supplant them, so that, as Mellor (p. 102) says, the use of weighed filter papers will soon be obsolete, as it should be now.

The crucible containing the precipitate is covered with a small (7 cm.) filter paper and placed on the shelf in the oven.[2] The paper prevents contamination by particles falling from the oven top, and at the same time allows the steam to escape. The regular crucible cover is laid aside in a clean place. The door of the oven is closed, the burner beneath it is lit and the temperature is brought gradually to 110° C., 130° C., or whatever may be required. It is held at this temperature for the requisite time by adjustment of the burner from time to time, if there is no regulator attached. A little practice soon teaches one the correct height of flame.

The crucible is then placed in the desiccator, its cover is put in place, and it is allowed to cool for weighing.

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[1] Blasdale, p. 154; Fresenius–Cohn, 1, pp. 112–120; Hillebrand–Lundell, pp. 96–99; Mellor, pp. 168, 183, 213, 219; Treadwell–Hall, pp. 32–41.

[2] The crucible may be placed (open) in a small beaker, and this covered with a watch-glass.

If the precipitate is collected in a paper filter it should always be ignited from a moist condition. If heating and ignition with paper or carbon changes the precipitate, the platinum Gooch or Munroe, or a vitreosil crucible should be used.

The practice, much recommended[1] and frequently used, of drying the precipitate and filter, then removing the greater part of the precipitate, burning the filter paper separately, and igniting the precipitate and ash, is one that, like weighed paper filters, should never be used. The manipulation is very apt, if not almost certain, to lead to the loss of some of the dry powder, and this antiquated method should be superseded by the use of the Gooch or Munroe crucible.

The ignition of the precipitate in a moist paper filter is a simple procedure, and is the one by far most frequently used in the analysis of rocks.

The free edges of the moist filter containing the precipitate in the funnel are loosened and then folded down all around over the precipitate. This is done with the platinum spatula, the end of which should not be soiled by the precipitate. In this way the mass of moist precipitate is completely inclosed in paper.

The funnel being in the left hand, the little package is gently loosened and lifted by the platinum spatula and is placed in the bottom of a previously weighed platinum crucible. This should, if possible, be not more than half filled by the package. This is laid down with the three-fold side uppermost, and is pressed snugly down, but without breaking the paper, and a channel being left for the exit of steam from beneath. The used tip of the spatula is cleaned on a small scrap of filter paper, folded once to cover the possible trace of precipitate from the spatula, the funnel is rubbed with it all around at the line of the filter edge to remove any precipitate that may possibly have crept up. The paper, folded up, is placed in the crucible alongside the main mass.

In this way the precipitate may be dried in the crucible without danger of loss from whirling up of powder or from handling of the crackly and somewhat brittle dried paper that is involved in the earlier method. Incineration of the filter will be complete.

The crucible, with the cover in place, is supported vertically in a triangle and heated over a rather low flame of a Bunsen burner. The appropriate conditions will vary somewhat, but for this stage of the drying the flame should be 5 to 7 cm. high and the bottom of the crucible 10, or better, 15 cm. above its tip. The object is to dry the moist mass of precipitate without boiling of the pasty mass or spattering against the sides of the crucible. One should be patient and heat with great caution to prevent this.

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[1] Blasdale, p. 154; Fresenius–Cohn, **1**, pp. 118–220; Treadwell–Hall, pp. 32–34. Cf. Hillebrand–Lundell, p. 96, who are opposed to the practice.

The much-used method of drying the precipitate and carbonizing the paper by heating the handle of the cover resting on the vertical crucible is to be discouraged. Besides being unnecessarily tedious, there is great probability of the flame gases entering the crucible and causing the presence of a reducing atmosphere.

When the mass is dry, and there are no more drops of water on the under side of the cover, the crucible is gently and gradually lowered, a little at a time. When doing this the ring on which the triangle rests should be steadied with the tongs, while the clamp is loosened and the ring lowered.

The paper is thus carbonized *very gradually*, which is an advantage; as paper carbonized at a low temperature is more easily incinerated than if carbonized rapidly and at a high temperature. The escaping vapors must never be allowed to ignite, as this may lead to loss of the powder through the slight explosion at ignition and the currents that are set up. Until the paper is wholly carbonized, as is shown by the pure black color, the bottom of the crucible should not be brought close enough to the flame to become red hot.

Ignition.—When the paper is entirely carbonized, the crucible is lowered and the flame is slightly raised, so that the bottom of the crucible is at a low red heat. The cover is slipped a little to one side to allow a little air to enter, the crucible being still vertical, and not on its side at this stage, as is often recommended. The red heat at the bottom is maintained until the paper is wholly burnt away, the flame being somewhat raised toward the last, but *never enough to envelop the crucible.*

One of the most serious of the usual faults in making an analysis is enveloping the crucible (covered or uncovered) in the flame. This is frequently done, but the careful analyst should never be guilty of this practice. The reasons for this statement are as follows: The crucible is apt to come into contact with the cone of unburnt gas, and so be attacked; there may be a reducing atmosphere within the crucible, which may lead to serious consequences, as with the ignition of phosphates; there will certainly be draughts in the crucible, which may carry away light substances, such as silica; the heat is needed, not at the top, but at the bottom of the crucible where the precipitate lies, and the hottest part of the flame is very near the top; and finally the use of such large flames is an example of the general fault of megalism or overdoing things.

If the carbon of the filter paper or that which penetrates the precipitate burns slowly, its combustion may be hastened by removing the flame and allowing air to penetrate the carbon. On reheating, combustion will usually be rapid. The under side of the crucible cover should always be examined to see that it is free from carbon. If this still adheres after the carbon of the paper is consumed it is burnt off by holding the cover convex side up in the platinum-tipped tongs above the flame for a few minutes.

In general, the crucible is ignited at a bright red heat (about 900° C.), with the crucible vertical, the cover very slightly to one side, and the flame *not enveloping the crucible.* This ignition may last for thirty minutes, but for many precipitates fifteen to twenty minutes will suffice. The flame is then turned off, the crucible allowed to cool below redness, and, while still warm, placed in the desiccator to cool before weighing. Until one has had experience as to the time of ignition, it is well, after weighing, to reheat for ten minutes, cool and again weigh, until there is no loss of weight. Indeed, it is always best to do this.

With some precipitates, especially where an oxidizing atmosphere is necessary, as with ferric oxide, the crucible is laid on its side on the triangle, not quite horizontal, the mouth toward one of the ends. The cover is leaned against it with the handle to one side, almost, but not quite closing it. If the end of the triangle is not twisted, a few notches may be filed along one of the ends to keep the cover from slipping. The flame is applied only to the lower end of the crucible, not near the mouth.

This position of the crucible is much recommended, but, in my opinion, *is not well adapted to most precipitates,* especially those (such as silica or calcium oxide) which are in the form of light powders, as the danger of loss from draughts is very great. The crucible and cover should never be placed in the irrational position sometimes figured.[1] The flame must always play on the base of the crucible, never around its mouth.

In igniting a precipitate in a Gooch crucible the procedure is much the same. If the crucible has a bottom cap, this is put on and the covered crucible is heated above a low flame as described above until the felt and precipitate are dry, after which it is ignited at a bright red heat. If there is no cap, the Gooch crucible is placed in a larger platinum crucible and is heated and ignited in the same way.

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[1] Fresenius–Cohn, 1, Fig. 77, p. 116; Gooch, Fig. 19, p. 76; Treadwell–Hall, Fig. 16, p. 39. These figures represent positions that are quite impossible or absurd.

Some precipitates, for example silica and alumina, may require heating by the blast burner. This is done after the crucible and contents have been heated at bright redness for fifteen minutes. In blasting, the crucible should be vertical, the cover very slightly slipped to one side (about 1 mm.). The flame of the blast should not be large and should be directed obliquely only against the bottom and lower fourth of the crucible. In blasting, especially, it is most important that the flame does not envelop the crucible.

For many purposes the Meker burner, which gives a hotter flame than the Bunsen, will take the place of a blast. Though it may take slightly longer to ignite the substance, there is less liability of loss in weight of the platinum through vaporization than if the blast is used. A small Meker is preferable to a large one, which gives much too large a flame.

If a good grade of filter paper is used, such as those recommended on page 53, the weight of filter ash may be neglected in the calculations, as it will fall within the other limits of error. The only general exception would be in the case of the precipitate by ammonia, for alumina, etc., when three or more 11-cm. filters are ignited. The combined weight of their ash may not be negligible in accurate work, and should be deducted from the weight of the ignited precipitate.

8. TITRATION[1]

In the ordinary course of rock analysis, volumetric operations are made use of only in the determination of iron oxides, and in some of the colorimetric methods for titanium, manganese, and chromium. They can be used also for the determination of other constituents, but this is not recommended in rock analysis, where gravimetric methods are preferred for the great majority of determinations. No full discussion of volumetric methods, or their principles, will be attempted here, but a few practical suggestions will be made that may be of use to the beginner.

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[1] The textbooks frequently cited throughout these pages, those of Blasdale, Fresenius–Cohn, Gooch, Hillebrand–Lundell, Mellor, Treadwell–Hall, and especially Kolthoff–Furman, describe the various procedures of volumetric analysis in more or less detail; they should be consulted by the student for the principles and much information that are not given in this book.

Volume-Burette.—Two types of burette are in general use, the volume- and the weight-burette.

The volume-burette in almost universal use is of the Mohr's form, the older ones devised by Gay-Lussac and by Geissler[1] being nowadays never seen in the United States, and they are not listed in the dealers' catalogues consulted by the author.

The tip of the Mohr's burette may be either straight or set at an angle, best at 90°, of the so-called Fresenius form. The stop-cock must be of glass, as a rubber pinch-cock (used with the straight tip) is inadmissible with solutions of permanganate. The most useful capacity is 50 c.c., graduated to tenths of one cubic centimeter. The burettes should be calibrated, best of the "M.C.A." specifications, and they should be consistent with the measuring-flasks used.

The burette must be perfectly dry before the standard solution is introduced, and it is well to rinse it out with a few cubic centimeters of the solution before filling. The standard solution should be taken from the stock bottle with a pipette, not poured out, as this last may disturb its titer. Before taking out any standard solution the bottle containing it is to be gently shaken, so that any drops of water that may have been deposited by evaporation on the upper walls may be washed down. The burette is filled to above the zero mark and is allowed to run out until the meniscus is level with this. The tip of the burette should be filled in doing this.

The glass stop-cock, whether of Mohr's form or of the weight-burette, should not be greased when using permanganate solution.[2]

The precautions to be observed in reading the position of the meniscus, so as to avoid the effects of parallax, are described by several of the authorities mentioned above. As we have, in rock analysis, to deal only with liquids that are transparent and light-colored,[3] the lower edge of the meniscus is to be used. For reading the position of this, I prefer a general illumination giving the effect shown by Fresenius.[4] The eye must be level with the meniscus, but such devices as a float or a vertical stripe at the back are generally neither necessary nor advisable. One can use a strip of white paper, with a straight edge uppermost, bent around the burette and with the ends of the straight edge meeting. This is moved up or down until the front and rear portions of the straight edge are in line with the lowest point of the meniscus.[1]

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[1] Fresenius–Cohn, **1,** Fig. 23, p. 48 and Fig. 24, p. 50.

[2] Cf. Mellor, p. 197. According to Lunge (cf. Kolthoff–Furman, Vol. Anal., **2,** p. 13) the action of the grease on permanganate may be neglected.

[3] The permanganate solution of proper strength for rock analysis is so light in color that the bottom of the meniscus can easily be seen through it.

[4] Fresenius–Cohn, **1,** p. 46, Fig. 19.

In reading a volume-burette, a few minutes must be allowed for the drainage of the liquid adhering to the walls above the meniscus, or the reading will be too high. The burette may be gently tapped to facilitate this. For all but the most accurate work there is no need for corrections for temperature.[2]

Weight-Burette.[3]—For accurate work the weight-burette has some great advantages over the ordinary form, which make it preferable for use in the determination of iron oxides. These advantages are:[4] No calibration is required; no correction for temperature changes is necessary; it is not necessary to wait for drainage; reading the position of the meniscus is not involved; the solution can be weighed accurately to 0.01 gram, whereas measurement to 0.01 c.c. is very uncertain.

The tip should be at right angles. The burette is provided with a hollow, ground-glass stopper, in which is a small hole, there being a similar hole in the neck. During weighing, the stopper is turned so that the two holes do not coincide, thus closing the burette. *Before titration the two holes are made to coincide,* so that air may enter and the solution escape. The glass protecting cap should be placed on the tip during the weighing

Before being filled the burette must be dry, and some of the solution (permanganate) to be used is shaken in the burette and allowed to run out. This serves to clean the burette and at the same time saturates the air within it with the vapor of the solution. The burette of appropriate size (100 c.c. or 50 c.c.) is filled nearly, but not quite to the stopper,[5] this is put into place, being so adjusted that the two holes do not coincide, and the protective cap is placed on the tip, great care being taken while doing this, that the plug of the stop-cock is not loosened. The burette is then wiped dry with a clean towel, and is weighed to the nearest centigram.[6] In carrying the burette to the balance-case it is well to hold the burette by the neck with the forefinger and thumb of one hand, and with a finger of the other pressing lightly against the cap, so that this may not slip off and be broken. The burette may be handled with dry fingers. In weighing, it is suspended by a loop of wire attached to it from the hook above the left-hand pan. After weighing, it is placed in the clamp with rubber-covered jaws, which are gently screwed up so as to hold the burette in place, but without danger of crushing it.

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[1] Cf. Kolthoff–Furman, Vol. Anal., **2**, p. 15.

[2] A table for these is given by Treadwell–Hall, **2**, p. 461.

[3] M. Ripper, Chem. Zeit., p. 793, 1892.

[4] Cf. E. W. Washburn, Jour. Amer. Chem. Soc., **30**, p. 40, 1908; R. S. McBride, Bur. Standards, **8**, p. 617, 1912; Kolthoff-Furman, Vol. Anal., **2**, p. 10.

[5] The graduations on the side serve as a guide to the rough measure of the amount of liquid used during titration; they must not be used, however, for measuring the exact volume.

[6] Kolthoff–Furman, Vol. Anal., **2**, p. 11.

Procedure.—To allow the liquid to escape, in working with either form of burette, the cock is best managed with the left hand, the right being used to stir the liquid in the iron titration. The sides of the plug and of the socket should be straight and strictly conical and well-fitting, so that they do not jam on turning. In turning the cock, care should be taken, on the one hand not to bear down so heavily as to cause the plug to stick in the socket, and on the other not to raise the plug so as to let liquid escape between the plug and socket. The tip should not be so high above the liquid as to cause drops to splash.

The liquid must be added cautiously, and after each addition the flask is rotated or the liquid in the beaker is stirred. Toward the end the addition must be drop by drop, great caution being needed not to overrun the end-point. When the total amount is known approximately, the first additions of the standard solution may be relatively large, but the end-point must be approached with some degree of caution. A single drop should be sufficient to cause this change, though in the titration for ferrous oxide the decision as to the end-point is complicated by the presence of hydrofluoric acid, which renders the color evanescent, unless boric acid is present, as we shall see.

More details will be found in the descriptions of the various methods in which a burette is used, those for ferric and ferrous oxides, and the colorimetric methods for titanium and manganese.

PART V

METHODS

1. General Course of Analysis

Before beginning the detailed descriptions of the methods for determining[1] the various constituents it will be advisable to state concisely what the course of an analysis is, in what separate portions the different constituents are determined, and the plan of separation, in order to obtain a general survey of the analysis, so that the details may be considered later with greater intelligence and knowledge of their relations to the whole analysis. In this summary, if there are several alternative methods that are described subsequently, only that one will be mentioned which especially recommends itself for general use, and which, in general, the author has adopted for his own work. [illegible] outline [illegible]

(*a*) Silica, alumina, total iron oxides, titania, lime, strontia, and magnesia are determined in a portion of 1 gram[1] which is usually called the *"main" portion.* The powder is fused with five times its weight of sodium carbonate, the cold cake is dissolved in hydrochloric acid, and the solution is evaporated to dryness, thus rendering the silica insoluble. The silica is filtered off; and in the filtrate alumina, ferric oxide, titania, and phosphorus pentoxide are precipitated by ammonia, with or without the addition of bromine water or ammonium persulphate to precipitate manganese. After filtration, the precipitate is dissolved in hydrochloric acid and reprecipitated by ammonia, and this is repeated if there is much magnesia present. The final precipitate is ignited and weighed, and is then brought into solution by fusion with potassium pyrosulphate. The melt is dissolved in water, the iron is reduced from the ferric to the ferrous condition by hydrogen sulphide, the excess of this is boiled off, and the total iron oxides are determined by titration with potassium permanganate. Titania is determined in the same liquid by the colorimetric method, which consists in comparing the intensity of color of a known volume of the liquid after oxidation by hydrogen peroxide, with that of a standard solution of titanium colored in the same way.

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[1] The phrase "to determine" is more appropriate than "to estimate"; the former is defined as "to ascertain definitely," and the latter as "to form a judgment regarding the value, etc., of" (Century Dictionary). The former is definite, the latter is approximate. Compare Mellor, p. 672, note 3.

[2] In analyzing rocks that are unusually high in alumina, lime, and magnesia, a smaller weight of rock powder may be taken.

The filtrate from the ammonia precipitate is precipitated with ammonium oxalate, the precipitate of calcium oxalate is dissolved and reprecipitated, and the lime is determined as such by ignition of the oxalate. Strontia may be determined in the weighed lime, obtained as above, by solution in nitric acid, evaporation to dryness, solution of the calcium nitrate by a mixture of ether and absolute alcohol, solution of the strontium nitrate in water, and precipitation of the strontium as sulphate after the addition of alcohol.

In the filtrate from the calcium oxalate the magnesia is determined by precipitation as ammonium magnesium phosphate, which, after solution and reprecipitation, is ignited. The magnesia is weighed as pyrophosphate.[1] The filtrate from this last operation is rejected.

The operations for the main portion are schematically summarized by Mellor.[2] The following is a simplified and slightly modified form of his statement. It is assumed that persulphate or bromine has not been added before the ammonia precipitation, that the small amounts of MnO distributed among the Al_2O_3, CaO, and MgO are neglected, and that the filtrate from the ammonia precipitate is not treated with H_2S to determine MnO. Solids are at the left, filtrates and solutions at the right. The constituents to be determined are in boldface type.

(*b*) Ferrous oxide is determined in a portion of powder of half a gram by solution in a boiling mixture of hydrofluoric and sulphuric acids, the operation being conducted in a well-closed platinum crucible. The contents of the crucible are transferred to water and titrated with potassium permanganate.

(*c*) Alkalies are determined in a portion of half a gram of specially ground powder which is effected by the Lawrence Smith

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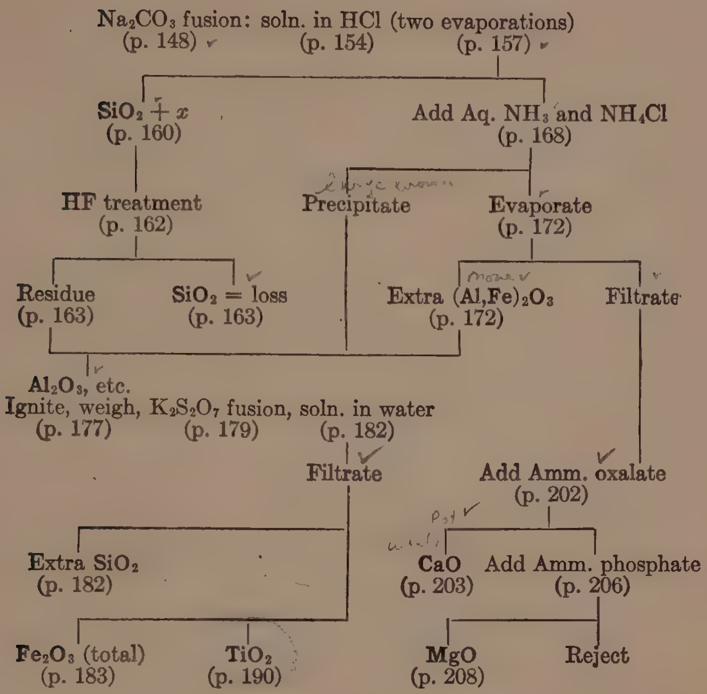
[1] The magnesia may also be precipitated as magnesium hydroxyquinolate, and weighed as oxide.

[2] Mellor, p. 242. See also Hillebrand–Lundell, pp. 50–52, with remarks on precautions to be taken in devising and using such schemes.


Na_2CO_3 fusion: soln. in HCl (two evaporations)
(p. 148) (p. 154) (p. 157)
$SiO_2 + x$
(p. 160)
Add Aq. NH_3 and NH_4Cl
(p. 168)
HF treatment
(p. 162)
Precipitate
Evaporate
(p. 172)
Residue
(p. 163)
SiO_2 = loss
(p. 163)
Extra $(Al,Fe)_2O_3$
(p. 172)
Filtrate
Al_2O_3, etc.
Ignite, weigh, $K_2S_2O_7$ fusion, soln. in water
(p. 177) (p. 179) (p. 182)
Filtrate
Add Amm. oxalate
(p. 202)
Extra SiO_2
(p. 182)
CaO
(p. 203)
Add Amm. phosphate
(p. 206)
Fe_2O_3 (total)
(p. 183)
TiO_2
(p. 190)
MgO
(p. 208)
Reject

method. The powder is intimately mixed with ammonium chloride and calcium carbonate, and heated under the proper conditions. After thorough leaching, the lime is precipitated by ammonium carbonate, and the filtrate from this is evaporated to dryness. The ammonium chloride is driven off by cautious heating, and the chlorides of sodium and potassium are weighed. The potassium is separated by chloroplatinic acid, and is weighed as chloroplatinate, the soda being determined by difference from the weight of the mixed chlorides.

(*d*) Total water is determined by Penfield's method in a portion of ½ to 1 gram. The powder is ignited in a dry glass tube sealed at one end, and the water is driven into the cool portion of the tube; the end containing the powder is drawn off, and the water is weighed in the remaining portion. The amount of hygroscopic water is deducted.

(*e*) Hygroscopic water is determined in a portion of about 1 gram by heating the rock powder in an oven at a temperature of 110° C. This portion may also be used afterward for the determination of other constituents, as P_2O_5, MnO, or ZrO_2, S, and BaO.

(*f*) Phosphorus pentoxide is determined by digestion of a portion of about 1 gram with nitric and hydrofluoric acids, removal of silica by evaporation to dryness, and subsequent precipitation as ammonium phosphomolybdate. This precipitate is dissolved in ammonia, the phosphorus is thrown down by magnesia-mixture as ammonium magnesium phosphate and weighed as magnesium pyrophosphate.

(*g*) Manganous oxide is determined in a portion of 1 gram, the rock powder being broken up by heating with sulphuric and hydrofluoric acids, the latter being driven off. In the filtrate the manganous salt is oxidized to permanganate by potassium periodate or by the use of silver nitrate and ammonium persulphate, and heating the liquid. The manganese in this solution is then determined colorimetrically, by comparison with a standard solution of manganous sulphate similarly treated.

(*h*) Total sulphur, zirconia, the rare earths, and baria may be determined in a portion of 1 gram. The rock powder is fused with sodium carbonate and the melt is leached with water. After acidifying the filtrate with hydrochloric acid, the sulphur is precipitated and weighed as barium sulphate. The zirconia is dissolved out of the residue insoluble in water by dilute sulphuric acid, and, after the addition of hydrogen peroxide, is thrown down and weighed as pyrophosphate by the addition of sodium phosphate. The rare earths may be determined in the filtrate from this precipitate. The barium remains as sulphate after solution of the zirconia. It is brought into solution by fusion with sodium carbonate, which converts it into carbonate, the melt is leached with hot water, and the residue is dissolved in hydrochloric acid. The barium is precipitated as sulphate, in which form it is weighed.

(*i*) Sulphur trioxide is determined in a portion of about 1 gram by digestion with dilute hydrochloric acid and precipitation as barium sulphate in the filtrate.

(*j*) For chlorine, a portion of 1 gram is digested with chlorine-free nitric acid, and the chlorine is precipitated in the filtrate by silver nitrate.

(*k*) Fluorine is determined in a portion of 2 grams by fusion with sodium carbonate, leaching with water, and precipitation of the filtrate with ammonium carbonate, the filtrate from which is precipitated with an ammoniacal solution of zinc oxide. In the filtrate from this a mixture of calcium carbonate and fluoride is precipitated by calcium chloride. and the calcium carbonate dissolved out by acetic acid, leaving the calcium fluoride, in which form the fluorine is weighed.

(*l*) A portion of from 2 to 5 grams is used for the determination of carbon dioxide. The rock powder is decomposed by hydrochloric acid in a small flask, and the carbon dioxide is absorbed in a weighed U-tube containing soda-lime, precautions being taken to keep the apparatus full of a current of air free from carbon dioxide, and to properly dry and purify the gas given off from the rock.

(*m*) For chromium sesquioxide 1 gram of rock powder will suffice, though a portion of 2 grams is preferable. After fusion with alkali carbonate and a little potassium nitrate, and subsequent leaching with water, the chromium is determined as chromate in the filtrate by a colorimetric comparison of a known volume of the solution with a standard solution of potassium chromate.

In regard to the weight of the portions which it is recommended to take for the various determinations, it should be borne in mind that they are intended for the great majority of rocks, but that in exceptional cases they are to be departed from according to the judgment of the analyst. For instance, in the analysis of iron ores, if a gram is taken for the main portion the bulk of the voluminous precipitate of ferric hydroxide will be so great that it cannot all be brought into one filter, and possibly not in two. The same is true of rocks high in alumina, such as anorthosite. Of such rocks, therefore, only half a gram of powder need be taken, even though extra care must be paid to the determination of other constituents. On the other hand, for the determination af alkalies in peridotites and other rocks in which their amount is extremely small, a gram or two of powder should be taken, instead of the half-gram which is usually sufficient.

The criticism is sometimes made that a portion of one gram is so small that it is inadequate to yield on analysis a just idea of the actual proportions of the several constituents in the mass of rock. It is, of course, generally true that the larger the amount of substance, within limits, which is taken for analysis, the greater will be the accuracy; that is to say, the more negligible will be the errors incident to the various operations in comparison with the mass taken.[1]

Practical considerations, however, such as the volume of precipitates and of filtrates, the practically manageable sizes of utensils, and the time involved in the different operations, set limits on the amount of the portion to be taken. The use of larger quantities permits (and therefore tends to encourage) careless methods of work without seemingly impairing the accuracy of the results.

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[1] Cf. Fresenius–Cohn, **1**, p. 71.

Furthermore, the criticism is unfounded, because if the specimen is well selected and enough of it is used for preparing the sample of rock powder, and if this is well mixed, one gram will be representative of the specimen.

We must compromise between the theoretical advantage of greater, and the practical advantage of smaller, weight of substance taken. Long experience of analysis has clearly taught what are the optimal amounts to be taken in particular cases, and the student should adhere to these whenever possible. It is, of course, assumed that the specimen of rock powder has been properly sampled and that the whole, and consequently a portion of it, is representative of the rock-mass.

2. TIME NEEDED FOR ANALYSIS

In answer to the question ''How long does it take to make a complete rock analysis?'' Hillebrand[1] states that, given ample and adequate laboratory facilities and apparatus, it is possible for an experienced and quick worker to complete an analysis of a series every three days, after the first is finished, barring delays. Although this is possible, the analyst is not generally dealing with a series of analyses, but is more concerned about the time needed for the completion of a single one, so that Hillebrand's statement does not really answer the question.

The time necessary for performing the separate parts of the various analytical operations are more or less fixed at minima by the conditions and circumstances of each. The times, however, may often be very largely controlled by the skill and judgment of the analyst. Thus, although the calcium oxalate precipitate must stand for a given number of hours, the careful and experienced analyst will take much less time than the beginner in its filtration, and will use much less water in washing it, and so lessen the time needed for the magnesia determination. Again, the skilful analyst will carry out several filtrations simultaneously, while other operations, such as ignitions and evaporations, are proceeding automatically. The beginner will find his time fully occupied with one filtration, and will probably have forgotten to utilize the time for automatic parts of other operations.

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[1] Hillebrand, Bull. **700**, p. 32; Hillebrand–Lundell, p. 659.

The beginner in analytical work has a strong tendency to use too large vessels and filters and to overwash precipitates; both of which lead to unnecessarily large amounts of filtrates. He also is very apt to ignite precipitates for an inordinate length of time. All such practices, which are mostly due to conscientious excess of care, not only increase the time needed for analysis, and in the aggregate greatly so, but make for lessening rather than for increasing the accuracy of the work.

The beginner is also very apt to leave a slow-running filtration "for a minute," forget it in the interest of some other operation, and thus lose time or get into difficulties, for example, with gelatinous precipitates.

Besides the general fundamentals of care, cleanliness, and conscientiousness, there are two short maxims that it will be well for the beginner to bear constantly in mind and conform to, if he wishes to complete an analysis in a reasonably short time. These are: "Be always on the job" and "Keep the sizes and volumes small."

The analyst should not be content to wait for each partial operation to be finished before beginning another, but should avail himself of the opportunities that present themselves for carrying on simultaneously as many separate operations as it is possible to carry out with success. The ability to do this naturally grows with experience in the purely mechanical execution, and also with judgment as to the best way of economizing time. It is not recommended that the novice should attempt very much in this way, and he will probably find that two or three operations are all that he can cope with simultaneously at the start. But he should constantly bear in mind the manifold possibilities in this direction and, with growing experience, avail himself of the various opportunities that present themselves.

Certain operations, such as evaporations and ignitions, proceed without attention, and while these are going on others which demand constant attention, such as the determination of FeO, may be carried out. Also, it is easily possible to carry out several filtrations simultaneously. With some practice, and a little thought, the number of different operations that may be conducted at the same time may easily reach six or more.

An actual example—not at all unusual—may be given of such simultaneous operations in the course of the analysis of two rocks carried out together. While the ammonia precipitate of the first was being ignited and the evaporations for K_2PtCl_6 and for P_2O_5 were proceeding, the filtrations of the first MgO precipitate and of the reduced solution for FeO, with that of the second SiO_2 and the $Mg_2P_2O_7$ (for P_2O_5) of another analysis, were carried out. One or two other evaporations and ignitions might have been proceeding at the same time.

The precipitates for the determinations of phosphorus pentoxide, sulphur, baria, and zirconia may be ready for filtration about the same time as the ammonium magnesium phosphate and the filtration of two of these precipitates may be carried out with that of the latter. Any such combination implies, of course, a liberal supply of utensils, so as not to be kept waiting for lack of those needed, and it also assumes a working day of seven or eight hours and that the analyst can devote several hours continuously at a time to the analysis.

To come to concrete figures, it is easily possible to finish an analysis involving the determination of eighteen or twenty constituents in five days, not necessarily consecutive, of seven or eight hours each without interruptions, and even in less time. Such an analysis can surely be made in six days without any special effort at economizing time. Indeed, a comparatively simple analysis in which a dozen constituents are to be determined, may be completed readily in four days without any sacrifice of accuracy, but this last is possible only in the hands of a rapid and experienced worker with the proper facilities.

In the following pages some suggestions are made as to the possibilities in the way of economizing the time taken for the analysis.[1] They are not intended to be final, but will serve merely as guides in laying out a plan of analytical work, and they are subject to modification to suit the exigencies of each particular case. In connection with them some estimates are given of the time that is needed for the several operations and determinations. These, again, must be regarded as only rough approximations, which will vary with different laboratory facilities and with the skill and experience of the operator. They will have to be extended somewhat when the analysis is made by a novice.

Assuming that we start Monday morning at nine o'clock, with about 50 grams of rock chips, these can be reduced to powder ready for analysis in less than an hour. Weighing out the crucible and the main portion (p. 146) will take about fifteen minutes. The main fusion with sodium carbonate (p. 148) is then begun at about ten o'clock, the time needed for the fusion and cooling being about one hour. During this time another separate portion can be weighed out, dried for half an hour at 110° C. for the hydroscopic water, and the portion mixed with sulphuric and hydrofluoric acids and started evaporating for the determination of manganous oxide (p. 251).

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[1] These suggestions and the times needed are based on an analysis (of a basalt) which was made with these points specially in view. The analysis was carried out in the usual way and without attempt at hastening it.

When the carbonate cake is cold it is transferred to the platinum basin. About one hour will be consumed in bringing this cake into solution. The evaporation of this liquid to dryness to render the silica insoluble will take until nearly three o'clock. During this time the determination of alkalies can be begun (p. 220). The special grinding and weighing out of the powder, and mixing with calcium carbonate and ammonium chloride, will take one-half to three-quarters of an hour, and the subsequent ignition another three-quarters of an hour, during which another portion is weighed out for phosporus pentoxide and its evaporation with nitric and hydrofluoric acid is begun (p. 247).

One should have time toward the end of the afternoon to wash the silica and begin the evaporation of the filtrate for the recovery of the extra trace of silica. This second evaporation may be continued until the close of the day (it will take about one hour and a half), or it may be continued on the steam bath over night. If that is not available it can be finished the first thing next morning. It will be seen that the first day is mainly one of decompositions and preparation.

On Tuesday morning the silica is first attended to. Washing the recovered silica, and the ignition and burning off of the small filter will not take more than half an hour, after which the heating and ignition of the silica begins, which will take an hour and a half to two hours

During the ignition of the silica, the precipitation with ammonia and the filtration of the precipitate (p. 168) should be begun. If three precipitations are necessary (as in this case), this will take nearly three hours, and will demand almost constant attention. During this time, however, the ignited silica can be weighed, and its evaporation with hydrofluoric acid started, the evaporation taking nearly an hour. This can be finished by the time the final ammonia precipitate is ready to put into the crucible with the residue from the silica and its heating is begun. It may be possible to get this alumina precipitate, if it is not large, dried and ignited by the end of the day.

When the ammonia precipitation is finished the filtrates are heated and the lime is precipitated with ammonium oxalate (p. 202). It is better, and involves no loss of time, to let the beakers with the calcium oxalate precipitates stand over night.

Time should be found this afternoon (Tuesday) to leach the cake from the alkali fusion, which has been soaking in a little water in the crucible over night, and also to precipitate the trace of lime in the solution with ammonium carbonate and filter off the precipitate. The evaporation of the filtrate containing the alkali chlorides can be begun and at least partly finished this day.

On Wednesday, the fusion of the ammonia precipitate in pyrosulphate (p. 179) will be completed. The time needed for this varies, being largely dependent on the amount of the precipitate, but it will often be possible to reduce and determine the total iron oxides on the same day that the fusion with pyrosulphate is begun. The alkalies can also be finished during this day.

The calcium oxalate precipitate is filtered off, redissolved and reprecipitated in the morning, and the lime is weighed after the precipitate has stood for two hours or so. Sodium ammonium phosphate is added to the filtrate to precipitate magnesia (p. 206), and the beakers are allowed to stand over night.

On Thursday, the magnesia precipitate can first be filtered off, redissolved and reprecipitated. It can be filtered off, ignited, and weighed late in the afternoon, or this can be done Friday morning. The alkalies are to be entirely finished this day, if they have not been done before, as should have been easily possible. The evaporation to dryness of the alkali chlorides will take one to two hours on the water-bath; their weighing fifteen minutes, and the evaporation of the chloroplatinate solution should not take more than an hour. The filtration in a Gooch crucible and the drying and weighing of the potassium chloroplatinate should be completed in less than an hour. The total time actively spent in these operations for determining the alkalies is small, not over three hours.

The total iron oxides (p. 183) can be titrated this morning, if this has not yet been done. The time needed for reducing the ferric to ferrous oxide with hydrogen sulphide will vary from one-half to three-quarters of an hour, the filtration of this solution may take another half hour, the expulsion of the hydrogen sulphide by boiling and the subsequent cooling of the liquid should be over in less than an hour, while the actual titration should be done in about twenty minutes, including the weighing of the burette twice.

When the total iron oxides have been determined, the colorimetric determination of titania (p. 190) can be carried out. All of this operation should not take more than one-half hour.

The determination of ferrous oxide should also be done on this day, though time might have been found for it before, as the operation should not take more than about one-half hour, during which, however, it will need constant and undivided attention.

It should also be possible to complete the manganese and phosphorus determinations this day, and sulphur and baria or zirconia, if these have been begun previously. Time can also be found for making the total water determination, an operation that will consume little more than half an hour.

The whole analysis should, therefore, be completed by Thursday evening, but, if not, Friday morning should see the completion of the various end determinations, such as the magnesia, manganese, phosphorus, zirconia, etc.

It will be found that there will be many intervals during which parts of the determinations of the minor constituents can be carried out, as these call for small volumes of liquid and so can be readily done in the gaps between the parts of the major operations.

3. Errors and Summation[1]

Character of Errors.[1]—It is well recognized that no analysis can be ideally perfect; that is to say, can yield results that show the percentages of the various constituents with absolute accuracy. No analyst is continuously, to say nothing of wholly, perfect in his manipulations; no piece of apparatus is entirely free from faults and no reagent is free from impurities; no conditions can be completely controlled; and lastly, no method for any determination is known that has not inherent in it some source or sources of error. The best the analyst can do is to strive to reduce to a minimum the various errors that may arise.

In connection with the descriptions of the various methods for the determination of the several constituents there will be discussed the particular errors inherent in each. It will be well, however, to present to the student some ideas on the general characters of analytical errors, so that he may deal more understandingly with the particular cases as they arise.

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[1] Blasdale, pp. 47–53; Hillebrand–Lundell, pp. 3–6, 654–658; Mellor, pp. 249–251; J. W. Mellor, Higher Mathematics for Students of Chemistry and Physics, pp. 510, 537, 1919; G. Tschermak, Neues Jahrb. Centralb., 1916, pp. 1–9; H. H. Robinson, Am. Jour. Sci., **41**, pp. 257–275, 1916.

Analytical errors may be referred to two broad groups, that may bt called the "operative" errors or errors of operation, which are incident to an operation or to the manipulation, and the "methodic" errors or errors of method, which are inherent and peculiar to each method.[1]

The "operative" errors are those such as are caused by the entrance of dust, spilling of drops and other mechanical losses, or too long-continued washing of precipitates.[2] The "methodic" errors include such as those due to coprecipitation of magnesia with alumina, the ready oxidizability of ferrous compounds, or the adsorption of salts by gelatinous precipitates.

Errors differ essentially in that the operative errors are due to causes outside the chemical and physicochemical factors of the analysis; whereas the methodic errors are dependent upon the chemical characters and peculiarities of the substances involved and on the conditions under which they are made to react.

That the one group may grade into the other, so to speak, is shown by such examples as the errors due to the over-washing of precipitates and to the adsorption of salts, in which correct results may be attained by balancing operative manipulations against peculiarities inherent in the method.

The occurrence of operative errors is brought about mostly by carelessness in manipulation, so that they are, or should be, almost entirely avoidable, they should always be eliminated as far as possible by the use of skill, dexterity, cleanliness, and thought.

Personal errors, such as those in reading burettes or the matching of colors, must also be taken into account. For our purpose they may be grouped with the operative errors, but, regarded as systematic errors, they are capable of mathematical treatment.[3]

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[1] This division is one of practicality and differs from the usual division into "accidental" and "systematic" errors, which are especially adapted to mathematical treatment. See Mellor, Higher Mathematics for Students of Chemistry, pp. 510, 537, 1919.

[2] Included among them are also "personal" errors and those due to impurities in reagents, inaccuracy in instruments, and the non-determination of constituents. Operative errors are discussed on pages 90–94.

[3] Cf. Mellor, Higher Mathematics, p. 537, note 1, 1919.

The methodic errors, on the other hand, are inherent in the particular methods, and so can seldom, if ever, be wholly eliminated. They can, however, be controlled and reduced to a minimum by sufficient knowledge and consequent attention to the proper conditions of reaction.

Some of the operative errors, such as the entrance of dust or the spilling of drops, are so obvious that nothing need be said of them to the intelligent and conscientious student. Others have been briefly dealt with in the section on operations, and some precautions have been pointed out by which they may be avoided. In the subsequent part of this book, in general, the operative errors will be assumed to be known and guarded against, and only those of a methodic character will be considered and discussed.

Direction of Errors.—The characters of the probable systematic errors to which the determinations of the several more important constituents are subject will be discussed in connection with the descriptions of the various methods. It may be of interest and use to the student to summarize very briefly the probable direction of *methodic* errors [1] of the more important constituents, whether plus or minus; that is, whether, because of them, a careful worker may be prepared to expect a result to be higher or lower than the truth.

Dittrich[2] has investigated this subject as regards alumina, ferric oxide, lime, magnesia, soda, and potash. Some of his methods were poor and one-half of the analyses were carried out by incompetent assistants, in itself one of the most usual sources of error, so that his results are of little value or significance. Robinson [3] has tabulated the probable direction of error for the more important constituents, basing his conclusions on many analyses made by several analysts according to the methods given by Hillebrand. Some very instructive comments on a large series of analyses of samples of the same argillaceous limestone are given by the Committee on Uniformity in Technical Analysis.[4]

The general conclusions to which the author has been led,[5] independent of this report, by consideration of the methods employed and from critical study of the many analyses of igneous rocks, are given in the following paragraphs.

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[1] It is understood that operative errors are not considered here.

[2] M. Dittrich, Neu. Jahrb., 1903, **2**, p. 69.

[3] H. H. Robinson, Am. Jour. Sci., **41**, p. 259, 1916.

[4] Jour. Am. Chem. Soc., **28**, p. 232, 1906.

[5] Washington, Prof. Paper **99**, pp. 13, 20, 1917.

Silica.—The errors incident to this determination are, on the whole, of small magnitude, with a tendency to the minus side. If a second evaporation for silica is made and that which is dissolved in pyrosulphate is recovered, they may be regarded as negligible; the more so because silica is, in the vast majority of igneous rocks, the constituent that is present in the largest amount, and its determination does not affect that of others. In judging analyses of inferior quality the author has found that the determination of silica (with that of lime) is one of those in which most confidence can be placed.

Alumina.—This constituent is more subject to error, both in magnitude and in variety, than any other of those determined in rock analyses. These errors may be of very serious consequence, despite the fact that alumina is usually the most abundant constituent next to silica, because its correct determination is of great importance in many mineral calculations.

The errors for alumina in the aggregate tend to be plus. Though there a few minus ones, these are generally much more than outweighed by those that are plus. This plus tendency is increased in incomplete analyses because alumina is determined indirectly by difference, so that the neglect of any of the constituents that are weighed with it will increase its apparent amount.

In the hands of incompetent or inexpert workers, the two chief sources of error, non-determination of constituents that are weighed with alumina and the coprecipitation of magnesia, as well as the difficulty of washing the precipitate, with the determination of alumina by difference, cause the figure for alumina to be almost invariably and inevitably high—often by several or many per cent. Even in the hands of careful workers, though alumina can be determined with almost as much accuracy as can most of the other constituents, there is a liability to variation or irregularity, with a plus tendency.

The determination of alumina must be regarded as the most unsatisfactory of all, even for the expert analyst, and, because of its importance, an accurate method for its direct determination is the most urgent need in the analysis of rocks.

Ferric Oxide.—Failure to reduce the ferric oxide completely to ferrous and loss through "creeping" in the pyrosulphate fusion tend to minus errors, whereas deterioration of the permanganate solution has the opposite effect. These sources of error, however, should be very small or negligible if the work is carefully done. Allen and

Johnston found, in their study of pyrite,[1] that the results of the gravimetric determination of iron are often high, sometimes by as much as 1 or 2 per cent of the iron present. This was caused by impurities in the ammonia, which had been kept in glass bottles. In general, however, the tendency with ferric oxide is toward minus, rather than plus error, and it is seldom serious with a careful worker if proper ammonia is used. If zinc is used for the reduction it is certainly plus because of the reduction of the titania.

Ferrous Oxide.—The chief source of error in the determination of this constituent is the liability to oxidation and the consequent difficulty in bringing it, unoxidized, into solution. This liability to oxidation and the difficulty of decomposition tend to cause low results. The only important factors of opposite tendency are the evanescent and uncertain end-point produced by hydrofluoric acid, unless boric acid is used, and the influence of manganous oxide in the permanganate titration. The plus tendency caused by organic matter, sulphides, and vanadium may be disregarded with most igneous rocks. On the whole, there is a tendency to minus error in the determination of ferrous oxide.

Lime.—If the ammonia is free from carbonate and the calcium oxalate is dissolved and reprecipitated, there are no serious systematic errors in the determination of lime. The weight of MnO brought down with the CaO is so small as to be negligible. Indeed, the figures for lime, as well as silica, can generally be taken with confidence as to their approximate accuracy, even in otherwise rather poor work. The error may be considered as having a very slight plus tendency, so small as to be negligible.

Magnesia.—Unless the analytical work is very careless, there should be little serious error in the determination of magnesia. The liability to precipitation of an ammonium magnesium phosphate of abnormal and variable composition, which tends to plus errors, must be eliminated by solution and reprecipitation under proper conditions. The retention of magnesia with alumina, due to insufficient ammonium salts, is possible and, indeed, probable with ignorant, careless, or hasty work, of which, indeed, it may be considered to be one of the characteristics. This minus error may be of very serious magnitude. The weight of MnO brought down with the ammonium magnesium phosphate, usually somewhat greater than with the CaO, causes a slight plus error. With good analysts the error in magnesia may be considered as plus or minus, that is, probably negligible; with inferior workers it is almost always minus, and often very much so.

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[1] Allen and Johnston, Jour. Ind. Eng. Chem., **2**, p. 202, 1910.

Potash.—With both potash and soda, if the Smith method of decomposition is used (as is here assumed), there is some tendency to minus error, chiefly because of retention of alkali chloride in the fusion cake through incomplete leaching. This should, however, be very small. The plus error due to alkali in the calcium carbonate is easily eliminated by making the proper correction, as should always be done if the carbonate is of such poor quality as to call for it. The presence of ammonium chloride in the air of the laboratory also leads to a plus error and should be guarded against. Errors due to other causes are so small in good work as to be negligible. On the whole the error tendency in potash might be regarded as negligible, but with a slight leaning toward plus, because of the presence of ammonium chloride in the laboratory air.

Soda.—The remarks just made in connection with potash, as to errors due to incomplete washing and to alkali in the calcium carbonate, apply equally to soda. As the amount of soda is generally greater than that of potash, and as it is determined by difference, these errors may be somewhat magnified with soda. The general tendency is the same as with potash. In his experience, the author has found both the alkalies to be among the most accurately and consistently determinable of the rock constituents.

Water.—Unless the rock is high in ferrous oxide and the water is determined "on ignition," there are no notable errors in the determination of water, either "combined" or "hygroscopic." The amounts are usually so small, and this constituent is as a rule so unimportant, that the errors may be regarded as insignificant.

Titania.—If the colorimetric method is used, the errors in the determination of titania are small and, because of the generally small amounts present, are seldom serious. Because of the bleaching effects of hydrofluoric acid and alkali sulphates, as has been pointed out by Merwin, there is a tendency toward small minus error. The errors involved in the gravimetric methods are small, but probably on the plus side.

Phosphorus Pentoride.—The errors incident to the determination of this constituent are so seldom serious, and the usual amounts in most rocks are so small, that they may be considered as insignificant. The tendency, if any, is toward very slight plus error.

Manganous Oxide.—If the colorimetric method is used the errors in the determination of manganese are negligible, particularly as the amount present is almost always very small. If the basic acetate method is used and the analyst is not expert, there is a decided tendency to plus error, which may be of both relatively and absolutely large magnitude.[1]

In the determination of the minor constituents the possible errors, though sometimes relatively great, are usually of such slight absolute importance that their directions need not be considered here. As Hillebrand remarks of the rarer constituents: "It is often more important to know whether or not an element is present than to be able to say that it is there in amount of exactly 0.02 or 0.06 per cent."

Limit of Error.[2]—Inasmuch as no determination can be expected to yield perfectly accurate results, or to be exactly reproducible on duplicate analysis, except by chance, we must assume some limits for the possible variation on either side of the truth, such that values falling within them may be regarded as satisfactory and consistent with good work. These limits may be called "allowable."

In attempting to allot the allowable limit of error for each constituent, regard must be had to its amount in any given case. Assuming that the allowable error is ± 0.60 per cent of the rock, which may not be quite correct, but is near enough for the present purpose, we might allot this proportionately among the chief constituents somewhat as follows: Taking, for example, the composition of the average igneous rock,[3] we would obtain these figures: $SiO_2 \pm 0.35$, $Al_2O_3 \pm 0.10$, $Fe_2O_3 \pm 0.03$, FeO, MgO, CaO, and $Na_2O \pm 0.3$, $K_2O \pm 0.02$, H_2O, TiO_2, P_2O_5, and $MnO \pm 0.01$. These are based on the assumptions that the errors may be all in one direction and are roughly proportional to the amount of each constituent.

We cannot, however, always expect such close agreement in duplicate determinations of the less abundant constituents as is implied by these figures. The matter is further complicated by the varied differences in difficulty and possible exactness that condition the several determinations, particularly as some of the errors may probably compensate each other to some extent.

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[1] Cf. Hillebrand et al., Jour. Am. Chem. Soc., **28,** p. 233, 1906; E. V. Shannon, Jour. Washington Acad. Sci., **17,** p. 451, 1927.

[2] Cf. Hillebrand, Bull. **700,** p. 30; Hillebrand–Lundell, pp. 654–658; Mellor, pp. 245–248; Dittrich, Neu. Jahrb., 1903, **2,** p. 69; Hillebrand et al., Jour. Am. Chem. Soc., **28,** pp. 223 ff., 1906; G. Panebianco, Riv. Min. Crist. Ital., **50,** p. 32, 1918.

[3] Clarke and Washington, U. S. Geol. Survey Prof. Paper **127,** p. 16, 1924.

Without going into a full discussion of this subject, and disregarding the various details that are peculiar to the several constituents, we may provisionally assume the figures given below as the allowable limits of error for constituents that are present in about the amounts mentioned.

It will be understood that the limits mentioned are in *percentages of the whole rock,* not of the amount of each constituent.

These allowable limits of error are: For SiO_2 and others that amount to 30 per cent or over, from ±0.10 to ±0.15; for Al_2O_3 and others that amount to from 10 to 30 per cent, ±0.05 to ±0.10; for constituents that amount to from 1 to 10 per cent, ±0.03 to ±0.05.[1]

These figures are but approximate suggestions, based on experience in the analysis of rocks and in the critical judging of rock analyses. They mean that duplicate determinations should not differ from the mean by more than these amounts, although it is very desirable, and usually quite possible in good work, that they fall well within them.[2]

The differences may, under peculiar conditions or with peculiar rocks or minerals, and with certain methods, be somewhat greater than those mentioned, without reflecting seriously or at all on the quality of the analysis; but such cases are to be judged only by the experienced analyst. The student should not think that the somewhat liberal latitude here given in these allowable limits of error justifies him as an excuse for poor work. He should, on the contrary, endeavor to make his analyses so that the difference between duplicate determinations, if they are made, falls within the limits thus allowed.

In order to check his errors, and so be in a position to correct them, the novice should make duplicate analyses throughout, until he becomes familiar with the methods and the manipulations, and by repeated close agreements may place justifiable confidence in his single determinations.[3] This will, at first, involve more labor and the turning out of fewer analyses in a given time; but the increased confidence in the results will much more than compensate in the end. An analysis in which the analyst himself cannot place implicit confidence is not only of little use, but is positively dangerous, for others, to whom there may be evident no reason for doubting the data; and such work will eventually and inevitably reflect injuriously on its maker.

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[1] These are in substantial agreement with the figures of Dittrich, Neues Jahrb., 1903, II, p. 81.

[2] The student will find many such examples among the mineral analyses by Penfield and many others in the 3rd, 4th, and 5th series of the American Journal of Science, and some of rock analyses in U. S. Geol. Survey Prof. Paper **99.** An excellent example, with comments on other work on the same material, is that on p. 229, Jour. Am. Chem. Soc., **28,** 1906.

[3] Robinson (Am. Jour. Sci., **41,** pp. 266, 273, 1916) and Hillebrand-Lundell (p. 658) also stress the importance of making duplicate analyses.

As regards duplicate determinations, however, it must be remembered that close correspondence in two determinations by the same method is not, in itself, conclusive proof of correctness. It is possible to obtain closely concordant or practically identical results on repetition by poor as well as by good methods; for if the same errors are made, and to about the same amount, in duplicate analyses, the figures in each may agree closely and yet be far from the truth. Penfield[1] and Mellor[2] have some sagacious remarks on this subject.

At the same time, if poor methods are used or if the analyst is incompetent, the chances are decidedly against obtaining duplicate results that are so closely concordant as to be satisfactory, particularly if operative errors have been committed; so that, if the methods are good and the analyst is competent, duplicate figures that agree well with each other justify, on the whole, a high degree of confidence in their correctness.

Summation.[3]—In the ideally perfect analysis, of course, the summation will be exactly 100 per cent; but in practice, as is well recognized, this result is seldom obtained, and if so it must be regarded as due to the compensation of different plus and minus errors.

As Hillebrand has stated, "A complete rock analysis which foots up to less than 100 per cent is generally less satisfactory than one which shows a summation somewhat in excess of 100. This is due to several causes. Nearly all reagents, however, carefully purified, still contain, or extract from the vessels used, traces of impurities, which are eventually weighed in part with the constituents of the rock. The dust entering the analysis from first to last is very considerable, washings of precipitates may be incomplete, and if large filters are used for small precipitates, the former may easily be insufficiently washed."

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[1] S. L. Penfield, Am. Jour. Sci., **10**, p. 20, 1900.

[2] Mellor, p. 248.

[3] Various phases of this topic have been discussed by: Fresenius-Cohn, p. 168; Hillebrand, Bull. **700**, p. 30; Hillebrand-Lundell, p. 654; Mellor, p. 245; M. F. Connor, C. R. **12**, Cong. Geol. Int., p. 889; H. H. Robinson, Am. Jour. Sci., **41**, p. 259, 1916; Washington, Prof. Paper **99**, p. 21.

On the other hand, deficiencies in the summation may be caused by mechanical loss, such as through spilling of drops or blowing away of light powders; or by physicochemical factors, as the partial solution of slightly soluble precipitates, or the incomplete absorption of carbon dioxide. A low summation may also be caused by the non-determination of some constituent.

The correctness of the opinion of Hillebrand and other experienced analysts that the plus errors tend to surpass the minus errors is shown by Robinson's average summation, derived from 3391 analyses. This is 100.13.

The limits of summation below or above 100 per cent which may be considered allowable and consistent with satisfactory work are considered by Hillebrand to be 99.75 and 100.50, and by Mellor 99.50 and 100.50. For allowable limits appropriate to *first-class work* by an experienced analyst the author is *in accord with Hillebrand.* But for the usual run of analytical work one may be liberal and fairly extend these limits to 99.50 and 100.75,[1] though the lower limit is, as Hillebrand remarks, rather too low for first-class work, especially in view of the tendency to high summations.[2]

If the analyst obtains a summation between these limits he may consider his analysis to be satisfactory, provided that there is no reason to suspect that errors have been made which would compensate each other and that all the essential constituents have been determined. For the student must realize that a summation of nearly or exactly 100 per cent *is not conclusive proof of accurate work,* because of the possible balancing of plus and minus errors.

If the analysis foots up under the lower limit, especially in several analyses of a series of similar rocks, there is strong probability that some constituent has been overlooked, or that some systematic error has been committed. In this case, or if the summation is above 100.75, the analysis should be repeated in whole or in part. As Hillebrand remarks: "It is not proper to assume that the excess (or deficiency) is distributed over all the determined constituents. It is quite as likely, in fact more than likely, to affect a single determination and one which may be of importance in a critical study of the rock from the petrographic side."

There are several special cases of high or low summation that are connected with the determination of various constituents, which do not, in themselves, indicate inferiority of the analysis as a whole.

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[1] Cf. Washington, Prof. Paper **99**, p. 21.

[2] The limit 99.50, instead of 99.75, was adopted in Prof. Paper **99**, so as not to exclude many otherwise satisfactory analyses from the section of "superior" analyses in the Tables.

If water is determined by loss on ignition the summation will usually be lower than it would be were the water determined directly. This is because of the partial oxidation of the ferrous oxide in the rock, and a consequent gain in weight, the algebraic sum of the gain of this and of the actual loss of water producing an apparent amount of water less than that which is really present.

If the iron oxides are not separately determined, but are given as ferric oxide, the summation will be too high by one-ninth of the amount of ferrous oxide present; and, conversely, if they are given as ferrous oxide alone, the summation will be too low by one-tenth of the ferric oxide present.[1] This error is, of course, eliminated if both oxides are determined separately.

If the analysis shows that chlorine, fluorine, or sulphur (as sulphide) is present, an amount of oxygen equivalent to the amounts of these must be deducted, or the summation of the analysis will be too high by that amount. The oxygen equivalent of chlorine is 0.22 of its amount, that of fluorine 0.42, and that of sulphur is 0.43 if this is present only in pyrrhotite. As regards the sulphur of pyrite, the iron with which it is combined will be given as ferric oxide in the statement of the analysis, although Hillebrand has shown that the mineral is attacked by sulphuric and hydrofluoric acids to only a scarcely appreciable extent in the determination of ferrous oxide. Consequently the oxygen equivalent of sulphur in pyrite is 0.375, instead of 0.25, as it would be were its iron content determined as ferrous oxide.

To give an example of the application of these corrections: If the sum of an analysis is 100.28 and there is 0.54 Cl present, we must deduct $0.54 \times 0.22 = 0.12$, leaving 100.16 as the correct summation. The corrections for fluorine and sulphur will seldom be called for.

In the earlier days of analysis both chemists and petrographers were content with very poor summations, even with those which fell below 99.00 or above 101.00. It is to be regretted that the same complacency, though less often met with, is not quite extinct at the present time. The intelligent and conscientious analyst or petrographer should look upon such summations with the gravest suspicion, and reject or remake any analysis which thus furnishes evidence of such manifestly erroneous results, either throughout or in part of the analysis.[1]

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[1] The molecular weight of Fe_2O_3 is 160 and that of $2FeO$ is 144, the difference (the weight of one atom of oxygen) being one-tenth of the former and one-ninth of the latter.

4. WEIGHING OUT THE PORTIONS

There are two methods of weighing out portions of rock powder for analysis; these may be called the method by addition and the method by subtraction.

The *method by addition* is most generally used and serves best for all the rock portions, except that used for the determination of the alkalies. The previously ignited and cooled crucible (covered) is weighed to tenths of a milligram as described on page 96, and its weight is recorded.[2] A weight equal to that desired, say one gram, is added to the right-hand pan. The crucible and its cover are removed from the left-hand pan with the forceps, the crucible (uncovered) being placed on the table in front of the balance-case. About the right amount (one gram) of the rock powder is carefully poured from the specimen tube into the crucible, taking care to raise as little dust as possible and to see that none of the powder adheres to the upper sides of the crucible. The crucible is then replaced (using the forceps) on the left-hand pan, its cover is laid on, and the pans and arms are gently released. If there is not enough powder to slightly more than outweigh the added weight, a little more is added, or if there is too great an excess of powder, a little is taken out with the platinum spatula, the crucible being, in either case, removed from the pan and placed on the table, so that none of the powder may fall upon the pan. This is continued until there is in the crucible a weight of powder but slightly (say about one centigram) more than the added weight. The correct weight is then taken to one-tenth of a milligram, as before. With a little experience one is soon able to judge quite easily when there is about the right amount of powder, allowance being made for the different specific gravities of different rocks.[3] Also, one will soon be able to judge from the movements of the pointer whether the difference in the weight on either pan is great or not.

It is neither necessary nor advisable to weigh out exactly 1.0000 gram of rock powder, as is sometimes done to save the slight trouble in calculation. This is very time-consuming and the trouble taken is far more than that involved in calculating the percentage of a portion weighed to not exactly one gram.[1]

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[1] This subject is discussed at some length in Washington, Prof. Paper **99**, pp. 21, 24, 25.

[2] It is essential that the beam and the pans should be arrested before placing on or removing the crucible, its cover, and the powder.

[3] Thus, a one-gram portion of basalt powder is distinctly smaller than one of granite.

The *method by subtraction* is used for weighing out the portion for the alkali determination, as well as when substances have to be weighed out accurately to make up standard solutions or the solution of sodium oxalate to standardize the permanganate solution.

The uncorked specimen-tube containing the powder is wiped perfectly dry and is placed on the left-hand pan of the balance. It is best to support it in a light metal tube-stand, so as to prevent its rolling. In handling the tube during the weighing it is scarcely necessary to use a dry handkerchief, as little or no appreciable error is introduced if the fingers are perfectly dry.

When it has been weighed, the requisite weight (say one-half gram, as for alkalies) is removed from the right-hand pan, and an amount of powder about equal to this is very carefully poured out into the proper receptacle, which will be the platinum basin with the alkali determination (p. 224). This pouring must be done with the greatest care, and the mouth of the tube is to be held close to the bottom of the basin, to prevent loss of powder.

When about a sufficient amount has been poured out[2] the mouth of the tube is tilted up (still above the basin), and the sloping tube is gently rotated around its axis, and possibly tapped very lightly, to bring the remaining powder away from the mouth and toward the bottom of the tube without loss. The basin is covered with a watch-glass, and the tube, still uncorked, is weighed as before. The loss in weight is the weight of powder taken for analysis.

It may be necessary to pour out several additional small portions so as to get the amount that is needed. A small excess, say of a few centigrams, or even a decigram, will be of no consequence in the alkali determination. But if one has poured out too great an excess, this cannot be corrected by replacing some of the powder in the tube, because some of it would inevitably be lost. If this happens, all of the powder is to be replaced in the tube, the basin is wiped clean and dry, and the operation is begun over again, the tube being reweighed.

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[1] The argument is exactly that used against the so-called "rational" weighing (p. 98).

[2] The beginner would best proceed cautiously and pour out at first a portion that is evidently too small.

5. Fusion with Sodium Carbonate[1]

For the determination of silica, alumina, total iron oxides, titania, lime, and magnesia, in what is called the "main portion," decomposition may be effected by several fluxes, as has been mentioned on p. 99. Of these, anhydrous sodium carbonate (Na_2CO_3) is the one most often used. It is used exclusively, indeed, for this purpose by the chemists of the U. S. Geological Survey and, until recently, by the author. The latter now uses, as do the other chemists in the Geophysical Laboratory, the sodium carbonate monohydrate, ($Na_2CO_3 \cdot H_2O$), because it is much more readily obtainable pure than the anhydrous carbonate.[2] These will, therefore, be the only ones considered here.

The Fusion.—The method of fusion with sodium carbonate owes its usefulness to the fact that this reagent at the temperature of fusion decomposes the minerals present, forming silicate, aluminate, phosphate, and zirconate of sodium, and carbonate, silicate, and possibly aluminate, of iron, manganese, magnesium, calcium, and barium, all of which are readily soluble in hydrochloric acid.

About one gram of rock powder is generally used for this operation. A platinum or palau crucible of 30- or 35-c.c. capacity is selected. A smaller one is not appropriate on account of danger of loss through bubbling of the melted mass, as well as on account of the greater difficulty in loosening the solid cake. For this fusion, the sides of the crucible should have considerable flare, and one with vertical sides is unsuitable. The crucible used for this fusion must be hard and not easily dented or bent. It should, therefore, be of platinum alloyed with iridium or of palau, which the author has found to be far better than iridium-platinum for this fusion, as the cake loosens very readily from it.[3] Pure platinum is much too soft for this fusion, because of the great difficulty in extracting the cake.

Any loss in weight upon ignition is of no consequence here, as the crucible is not weighed both before and after fusion, and it may be reserved for this purpose.

The crucible is cleaned, ignited to bright redness, and after it has cooled below a red heat, is placed in the desiccator and allowed to cool. *When perfectly cold,* it is weighed with the cover on, the weighing being carried to tenths of a milligram by means of the rider, and the weight noted. This weighing is carried out according to the directions given on p. 96, and the weighing out of the rock powder is carried out in the manner described on p. 146.

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[1] Classen, **2**, p. 608; Hillebrand, Bull. **700**, p. 95; Hillebrand–Lundell, p. 719; Mellor, pp. 163–166; Ostwald, p. 218; Treadwell–Hall, pp. 418–419; L. Duparc, Bull. Soc. Franç. Min., **42**, p. 152, 1919.

[2] It should not be necessary to reduce the monohydrate sodium carbonate to a fine powder; if this is done the agate mortar must be used.

[3] H. S. Washington, Jour. Washington Acad. Sci., **11**, p. 9, 1923. Cf. page 35, above.

It is not necessary, indeed it is better not, to weigh out exactly one gram, which will take considerable time, but an amount varying from 0.9 to 1.1 gram should be taken, preferably a little more rather than a little less than one gram. With some practice it will be found easy to estimate with the eye when one has about the right amount.

The crucible (covered) and the weights are removed from the balance, and one of a pair of balanced 3-inch watchglasses is placed on the righthand pan, and a 5-gram weight placed on it. On the other watchglass, dry, powdered, anhydrous sodium carbonate, or sodium carbonate monohydrate, is placed by means of a dry horn spoon, which is kept for this purpose in the balance-case, and which must be carefully wiped off at the end of the operation. Enough is added or subtracted to counterbalance the other watchglass and the 5-gram weight. The addition or subtraction is to be done with the watchglass on the table, not on the pan, lest some of the carbonate fall on the latter. It is not necessary to weigh the carbonate accurately, but the difference should not be more than a few decigrams either way. It is usually stated that the amount of carbonate should be four times that of the substance taken, but it is found that a somewhat larger amount is advisable for proper fusion, and for very basic rocks as much as six grams may be taken advantageously, as with these decomposition is less easy. Even if the sodium carbonate monohydrate is used (which contains less sodium carbonate) these quantities should be ample.

The crucible is placed on a clean sheet of paper, the cover is laid to one side, and the greater part of the sodium carbonate is transferred to the crucible by means of the platinum spatula, care being taken that none of the rock powder is thrown out. About half a gram of carbonate should be left on the watchglass.

The procedure of mixing the rock powder with the sodium carbonate has been spoken of on page 100. As, however, this fusion is of prime importance, it is here described in detail.

The flux and powder in the crucible are thoroughly mixed by stirring them gently with the broad end of the dry platinum spatula, this being done so that there is no loss of powder. They should be so intimately mixed that the mass appears homogeneous to the eye, and particular care should be paid to getting the carbonate well down and around the corners, so that no patches of unmixed powder remain at the bottom, where they would be attacked slowly and with difficulty.

When the powders are intimately mixed and smoothed down, the spatula is cleaned of any adherent mixture by rubbing it on the portion of carbonate that remains on the watchglass. This portion is then added to the mixture in the crucible.

The covered crucible is then placed vertically on a triangle, and is heated at a height of about 10 cm. above a low Bunsen burner flame for five to ten minutes, so that any moisture may be expelled. If the monohydrate carbonate is used, the preliminary heating to expel water should be especially cautious.

The crucible is then lowered until the bottom is a faint red, and is kept thus for another five or ten minutes. The flame is then gradually raised until the mass is in a state of quiet fusion. If the operation is conducted with proper care and slowness all the carbon dioxide, formed by the reaction between the silicates and the carbonate, can be driven off quietly through the sintered mass without any spattering.

When the mass is molten the height of the flame and of the crucible above it are so adjusted that the mass is liquid and of a dull red (about 900° C.), but without any bubbling or spattering of drops onto the cover. The crucible is to be kept covered during the operation, except to examine the contents. This will demand some attention the first few times the fusion is done, but with practice and care the right conditions are soon learned. The mass is to be kept in this state of quiet fusion for at least thirty minutes, during which, in the case of most rocks, slow currents are observed to cross the red-hot liquid.

If the rock is very high in iron oxides, lime, or magnesia, even long-continued fusion will not render the mass perfectly clear and transparent, as the carbonates of iron, calcium, and magnesium form cloudy masses within it, so that the sodium carbonate within the crucible may appear to be not entirely fused.[1] This appearance, however, need cause no concern, as these carbonates are readily soluble in hydrochloric acid.

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[1] Hillebrand–Lundell (p. 708) state that carbonates of calcium, magnesium, and iron are seldom present in fusions carried out at 900° C. to 1000° C., still less at 1200° C. This is probably correct, and the turbidity may be attributed to oxides or silicates.

Some sodium carbonate will usually vaporize and condense on the under side of the crucible, but this is of no consequence. The under side of the cover, however, must be examined for small spattered drops, which are later to be melted by holding the cover, convex side up, over the flame for a moment.

When the whole operation from the first fusion has lasted three-quarters of an hour to one hour, and it is judged that decomposition is complete, the crucible is taken from the flame and placed on a clean, cool, flat surface of iron or polished stone. Such methods for quick cooling as using a blast of air, or dipping the crucible into water, are *never to be used,* as they injure the crucible and greatly shorten its life. Hillebrand recommends giving the crucible a quick rotary motion before placing it on the slab, so that the melt may be spread over the sides in a thin sheet. This has the advantage of rendering the subsequent disintegration more rapid, and also to some extent facilitates the separation of the cake from the crucible. It is not, however, necessary, especially if a palau crucible is used, and the author always cools the crucible and contents quickly but quietly by placing it on a small slab of polished granite.[1]

During the first moments of cooling the melt should be watched, and if bubbles or miniature craters are formed, this may be taken as evidence that the decomposition and the expulsion of CO_2 are not complete. In this case the whole should be remelted and kept at a bright-red heat for another fifteen minutes.

It is very important that the crucible and its contents be *thoroughly cold* before the removal of the cake is begun. The contents must be so cold that they separate either wholly or partially from the metal walls. If water is poured into the crucible before the cake is thoroughly cold, the removal of the cake will probably be difficult. It is always better to be patient during the cooling process and to allow the crucible to stand more time than may actually be needed, than to incur the possible annoyance of a cake which obstinately refuses to be extricated.

When a considerable amount of pyrite is present in the rock, it is necessary to oxidize the sulphur. This may be done by adding a very small pinch of potassium nitrate to the carbonates. But even a small quantity of this gives rise to effervescence, through reaction with the carbonates, and hence increases the possibility of loss by spattering. There is also danger of attacking the crucible through action of the nitrate. It is, therefore, better, after weighing the rock powder and before the addition of the alkali carbonate, to roast the rock powder for ten minutes in the open crucible at a very low red heat, insufficient to sinter, and far less than sufficient to fuse the rock. The mass can then be mixed with the carbonate and the fusion proceeded with, as described above. This will seldom be necessary.

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[1] This is shown at the extreme right in the frontispiece.

As a general rule, the cold cake will be of a bluish-green color, due to the formation of sodium manganate. It sometimes happens that rocks high in ferrous oxide, even if they contain considerable manganese, show in the cooled melt not a trace of the characteristic green, but only a muddy brown color due to disseminated ferric carbonate.

Hillebrand[1] attributes certain irregularities in the coloration to the presence of a reducing atmosphere within the crucible, under conditions that are little understood. It is more probable that it is brought about by the reducing effect of ferrous silicate. Thus it may happen that "two fusions made side by side or successively, under apparently similar conditions, may in one case show little or no manganese, in the other considerable." It is probable that all rock analysts have had similar experience.

Removal of the Cake.—Before describing the removal of the cake from the crucible, one or two points in regard to the crucible itself may be touched on. From a new or little used iridium-platinum crucible with the ordinary amount of flare, the extraction of the cake usually offers no special difficulty, if attention is paid to the small points mentioned above and given below. But after a platinum crucible has been in use for some time, especially when it is often heated over the blast, the bottom tends to drop, and so alters the shape of the lower part. The smooth, single, interior concave curve becomes a double, ogee-like one, and, being slightly convex inwardly, frequently gives rise to difficulty in removing the cake. When the crucible that is used for the carbonate fusion gets into this condition, it should be returned to the maker to be re-formed.

As all dents and other irregularities are sure to cause difficulty, the platinum crucible should never be allowed to fall or become dented. Above all, any squeezing or other violent pressure should be avoided in attempting to loosen the melt, as any such deformations will greatly decrease the usefulness of the crucible. Caution on these points may seem superfluous, but one so often sees battered crucibles in use in laboratories, especially in the hands of students, that reference to them may not be amiss.

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[1] Hillebrand, Bull. **700**, p. 96; Hillebrand–Lundell, p. 709.

All such difficulties are overcome by the use of a *palau crucible for the sodium carbonate fusion,* because the cold cake is almost invariably easily loosened from this by the process described below.[1] Therefore, it is assumed that a palau crucible, or at least an undamaged, bright, iridium-platinum crucible, is used.

The thoroughly cold crucible containing the cake is placed on a triangle on the ring-support and is one-third filled with water.[2] After standing for a few minutes, to allow the water to creep below the cake, it is gently heated over a *small* flame. The flame is cautiously applied, especially around the edges of the cake, boiling being avoided as likely to lead to loss. After the edges are freed, the bottom is gently heated, when, under favorable circumstances, the cake loosens. If this first operation is not successful, the fluid is carefully poured out into the platinum basin, any drops running over the edges being washed into the basin with a little water from the wash-bottle. The crucible is then again one-third filled with water, and the operation is repeated. Two or three repetitions will usually be sufficient to attain the object. An undamaged, smooth crucible, patience, and gentle heating are the prime requisites for success in this operation; the opposites are disastrous.

When the cake is loosened it is transferred with the spatula to the platinum basin. It is well to place the cake in the basin with the bottom up, as this will aid in the subsequent solution in acid by the automatic movement of the cake through the release of gas bubbles. The crucible is washed slightly so as to transfer any loose particles to the basin. Small fragments of the melt may still adhere to the sides of the crucible, but these will be removed later. The crucible is therefore covered and laid aside. The platinum basin containing the cake is then one-third filled with water, and covered. It is not necessary nor is it a saving of time to disintegrate the cake by heating with water before adding the acid, as was recommended in the previous edition.

If the cake should prove obstinate and refuse to loosen from the crucible one of two methods may be adopted. The one preferred is to place the crucible on its side in the basin, filling this with water about one-third full (enough to cover the cake), and to heat gently until the cake is dissolved in the acid added later. The crucible is then lifted out of the basin by means of a stirring rod, and thoroughly washed, inside and out, while held on the rod above the basin, the washings, of course, falling into this.

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[1] Cf. Washington, Jour. Washington Acad. Sci., **11**, p. 9, 1921.

[2] The cake must be covered at least 0.5 cm. ✓

The alternative method is to dissolve and disintegrate the cake in the crucible with successive small portions of water, heated over a low flame or on the water-bath. The portions are to be poured into the platinum basin. This is rather tedious and requires attention if done over a low flame. It also is apt to lead to loss. The hydrochloric acid is then added, as below.[1]

Solution of the Cake.—If the cake is green, chlorine will be evolved on the addition of hydrochloric acid, through reaction with the manganate, and will attack the platinum. To avoid this a cubic centimeter of alcohol (either methyl or ethyl) is added to reduce the manganate.

The platinum spatula is washed with water into the basin and laid aside in a clean place. The basin is covered with a watchglass, which should project about one-half inch on all sides. This is, of course, placed with the *convex side down,* as must always be done with covering watchglasses.[2]

A few drops of acid are poured on the under side of the crucible cover, to dissolve any drops that may have spattered from the fusion, and washed into the crucible with a little water. A few cubic centimeters of dilute acid are then poured into the crucible to dissolve any adhering portions of the carbonate, and the covered crucible is laid aside.

Then 15 or 20 c.c. of concentrated hydrochloric acid are measured out into a 25-c.c. measuring-cylinder with lip, and poured very gradually into the basin through a small funnel, the end of which has been somewhat drawn out and bent at an angle of 120°, so as to project into the basin under the cover through the lip opening. This addition of acid should be very gradual, by a few drops at a time at first, so as to allow the effervescence to be as gentle as possible. It is also well to let the acid flow down the side of the basin below the lip, so that the drops thrown up by the first, somewhat violent, effervescence may be diverted away from the lip-opening. A pink blush, due to $MnCl_2$, indicates the presence of considerable manganese.

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[1] These removals have never been necessary for hundreds of fusions in the author's laboratory when a palau crucible has been used. They have sometimes been necessary with an iridium-platinum crucible, and almost invariably with one of pure platinum.

[2] This caution may appear to be superfluous, but the author has seen students place the watchglass with the convex side up.

The basin (covered) is heated on the water-bath to dissolve the cake in the hydrochloric acid. This solution is hastened by cautiously raising the cover and holding it horizontally a short distance above the basin while the cake is gently rubbed with the end of the spatula to remove the insoluble crust. Toward the end, when effervescence has about ceased, the cake may be broken up with the spatula.

When all effervescence has ceased in the basin, this is removed from the water-bath, and the drops on the watchglass cover are rinsed down into it, the glass being held vertically with the part downward that has been next to the lip and near the surface of the liquid in the basin. The rinsing is to be repeated several times, the stream being so directed as to cause the water to flow over all the wetted surface from top to bottom. The watchglass is laid aside, and the sides of the basin above the liquid are washed down by a gentle stream from the wash-bottle, the basin being slowly rotated to facilitate the operation. One complete washing down all around will be sufficient. The contents of the crucible are then added, and this and its cover are rinsed several times into the basin. When the operation is complete, if care has been used to avoid an inordinate amount of wash-water, the basin should be little more than half full.

As a little silica adheres persistently to the crucible the inside of it is to be rubbed with a small piece of moist filter paper, which is then dropped into the basin. This is disintegrated by the acid during the evaporation.

The platinum spatula is then put into the basin, resting in the lip, and this is placed uncovered on the water-bath for evaporation. The fluid should be clear and contain no solid except possibly some light particles of silica. There may be a few small black particles of magnetite or ilmenite present, which will dissolve in the hot acid.[1] But if small, hard, gritty particles are felt, by the spatula, at the bottom, the fusion has not been successfully carried out to complete decomposition of the rock, and the contents of the basin should be rejected, another portion of rock powder weighed out, and the whole operation of fusion with sodium carbonate is to be gone through with as before. This should never happen, and is easily avoided by sufficiently prolonged fusion with the sodium carbonate.

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[1] If they do not, they will be brought into solution by the pyrosulphate fusion later.

6. SILICA[1]

The fluid in the basin now contains all the rock constituents in solution as chlorides, except the silica, most of which is in solution as soluble silicic acid and also as insoluble particles. Our first object is to *render the silica insoluble* and thus separate it from the other constituents, so that it may be weighed. This is effected by evaporation to dryness, whereby the silica is rendered insoluble in water.

Errors.—It has been shown by many chemists that a single evaporation does not render all the silica insoluble; so that two evaporations are necessary for accurate work. Prolonged heating of the salts at 110° C.–130° C. is apt to allow some of the silica to be dissolved in the hydrochloric acid used, as well as to increase the impurities in the silica. This is due to recombination of the silica with some of the bases, mostly either with magnesia or with soda.

Complete dehydration of the silica is somewhat uncertain and is apt to be incomplete, and unless the silica is ignited at a very high temperature it is apt to be hygroscopic. Blasting for twenty minutes or so is therefore generally recommended. Although this may be advisable, it is apt to cause loss in weight of the crucible, and for general work the author finds that strong ignition over a good Meker flame for thirty minutes or more (to constant weight) gives accurate results.[2]

Although a second evaporation in the filtrate from the dehydrated silica is recommended by Hillebrand, Lenher and Truog, and other authorities, yet the author believes that its importance is overrated. Experiments and experience in his laboratory indicate that the silica recovered from a second evaporation is usually very small, from 1 to 4 milligrams, and sometimes only a few tenths of one milligram[3] and that the amount that is recovered from the pyrosulphate fusion is about what may be lost by only a single evaporation.

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[1] Classen, **2**, pp. 605–611; Fresenius–Cohn, **1**, pp. 509–511; Hillebrand, Bull. **700**, pp. 97–105; Hillebrand–Lundell, pp. 720–726; Mellor, pp. 166–167; Treadwell–Hall, **2**, pp. 415–417; Lenher and Truog, Jour. Am. Chem. Soc., **38**, p. 1050, 1916; and ibid., **39**, p. 2360, 1917.

[2] Hillebrand (Bull. **700**, p. 102) and Hillebrand–Lundell (page 724) urge the use of a blast for ten or thirty minutes, contrary to the experiments of Lenher and Truog (Jour. Am. Chem. Soc., **38**, p. 1060, 1916) who obtained good results with a Meker burner heated to constant weight.

[3] For studies on this matter see: Hillebrand, Jour. Am. Chem. Soc., **24**, p. 362, 1902; Lenher and Truog, Jour. Am. Chem. Soc., **38**, p. 1058, 1916; L. Duparc, Bull. Soc. Franç. Minéral, **42**, p. 159, 1919.

However, in deference to general practice, it is best to evaporate the first filtrate, and also to recover the silica from the pyrosulphate fusion. The time involved in this second evaporation is considerable and, in the author's opinion, is not justified in view of the fact that the amount of silica recovered is so small as to be quite or almost negligible, and that silica is the most abundant constituent of the rock.

A small amount of silica adheres strongly to the basin and will be lost if it is not rubbed off. It would appear to be almost impossible to remove this silica from porcelain with a "policeman,"[1] or a piece of filter paper.

Practically all the silica that is not rendered insoluble in the main evaporations is precipitated with the alumina, and must be recovered from the solution of the fusion of the ammonia precipitate in pyrosulphate, though a little of it is lost here, as silica is slightly soluble in this reagent. The amount, however, is always very small.

The weight of silica must always be corrected for the impurities that it invariably contains, by evaporation with hydrofluoric acid.

From the possible errors just given it may appear that the correct determination of silica is so fraught with difficulty and uncertainty as to be probably unsatisfactory. This conclusion, however, is not borne out by the facts. In the first place, the actual error caused by each of these possible sources of error is generally very small, with the exception of that due to impurity in the silica, which must be eliminated, however, by evaporation with hydrofluoric and sulphuric acids. Secondly, the errors apply to that constituent which is present in by far the largest percentage in the great majority of igneous rocks, and so they are of comparatively insignificant influence. Indeed, much critical study of the character and value of rock analyses has led the author to the conclusion that, in analyses not of the best quality, the figures for silica, and for lime, are more likely to be correct than those of any of the other constituents.

Separation of Silica.—To render the silica insoluble, the solution in hydrochloric acid of the cake from the sodium carbonate fusion is evaporated to dryness in the platinum basin.[2] This is carried out on

[1] Cf. Hillebrand, Jour. Am. Chem. Soc., **28**, p. 232, 1906.

[2] A good quality (such as Royal Berlin) porcelain basin may be used for the evaporation of silica. Cf. Lenher and Truog, Jour. Am. Chem. Soc., **38**, p. 1061, 1916; Hillebrand, Bull. **700**, p. 100; Hillebrand–Lundell, p. 720. Porcelain has the disadvantages that the evaporation takes much longer time than in platinum, the difficulty of completely removing the silica, and the possibility of the glaze being attacked. On the other hand, no platinum is introduced into the liquid from the action of ferric chloride on the platinum. A glass basin must never be used.

the water-bath until no more fumes of hydrochloric acid are given off and the mass appears to be perfectly dry, the yellow color of the moist salts changing to a pale brown. During the last stages it is well to break up the gelatinous mass occasionally with the platinum spatula, which is kept in the basin, so that the water and hydrochloric acid may pass off more readily. When the mass becomes crystalline, the lumps may likewise be broken up, but this should be done cautiously to avoid loss by flying off of particles of the salts.[1]

It is necessary that the salts be dry, but the salts should not be heated or baked for some time at a temperature of 110° C. or 130° C., as is recommended by some. This *should never be done,* because silicates are apt to be formed that are soluble in hydrochloric acid and so lead to passing of silica into the filtrate. The prolonged heating at the higher temperature will also add considerably to the impurities in the silica.

The salts are, therefore, heated on the water-bath for an hour after the mass is dry.[2] The salts, when cool, are moistened with 5 c.c. of concentrated hydrochloric acid, to dissolve the basic salts of aluminum, iron, and magnesium that have been formed during the evaporation, and the salts adhering to the spatula are also moistened with the acid. The salts should be made only pasty with the acid, as silica is appreciably soluble in strong hydrochloric acid. The pasty mass is mixed thoroughly with the spatula, some of it being rubbed around the line that marks the original border of the liquid, where a line of strongly adherent silica is apt to be formed.

Water is now added from the wash-bottle, the stream washing down the sides of the basin. About 100 c.c. of water in all should be added. The spatula is rinsed off into the basin, and is cleaned with a bit of filter paper which is dropped into the basin, because a little silica (only visible when the spatula is dry) adheres to it persistently. The basin should not be more than one-third, at most, full of liquid.

A glass stirring-rod, about one inch longer than the diameter of the basin, is placed in it, and the contents are heated on the water-bath or over a low flame, with constant stirring, until the chlorides are entirely dissolved and only insoluble silica remains. This is indicated by the absence of gritty particles of salt on feeling with the rod.

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[1] Mellor (p. 76, note 3) suggests the addition of a little alcohol before drying, to hasten the process. This is rather advantageous but is not necessary.

[2] Nothing is gained and time is lost by more prolonged heating. Cf. Hillebrand, Jour. Am. Chem. Soc., **24**, p. 367, 1902; Hillebrand–Lundell, p. 721.

While the solution of the chlorides is being effected at a gentle heat the filter may be made ready. A 9-cm. filter and a 6½-cm. funnel are used, and the filtration is carried out as described on page 104, a 400-c.c. beaker being taken to catch the filtrate.

When all the liquid and silica that will pass readily with it have been brought on the filter, the basin is gently rinsed with a little cold water from the wash-bottle, the silica adhering to the sides being washed down to the bottom, and the liquid and as much of the silica as possible are poured into the filter as before. When the filter is empty, the basin is held in the left hand, above the filter, with the stirring-rod across it and resting on the lip, the end of the rod an inch or so beyond, and the rod kept in place by the tip of the left forefinger. A gentle stream of water is then directed against the now uppermost side of the basin, so as to wash the silica into the filter, and at the same time rinse the basin. When the filter is nearly full the liquid is allowed to empty and the operation is repeated until the silica is thoroughly washed and all the silica is brought into the filter as far as possible without too many rinsings. The stirring-rod is washed off into the beaker.

H_2O

For washing the silica the author uses cold water, that is, at room temperature, and a little hydrochloric acid, about 5 per cent, is to be added to it. This addition is important because very dilute solutions of salts of iron and aluminum, either hot or cold, hydrolyze readily and throw down basic salts that contaminate the silica. It has happened in the author's experience that the silica became brick-red on ignition, from the iron present, when it was washed with *hot* water that contained no hydrochloric acid.

Lenher and Truog[1] and Hillebrand-Lundell (p. 721) recommend *hot* water containing 5 per cent of acid. But the difference in solubility of sodium chloride in hot and in cold water is very small and the solubilities of calcium and magnesium chlorides are so great that cold water should be practically as effective as hot for removing the salts. In either case, a little hydrochloric acid is to be added to the wash-water.

When the liquid has ceased to drop from the last rinsing of the basin, the platinum basin is substituted for the beaker beneath the funnel, taking care to lose no drops from the latter during the change. The contents of the beaker are poured into the ~~basin~~, and the beaker is rinsed two or three times, not more, the rinsings going also into the basin. The beaker and basin are then interchanged once more, and the stirring-rod is placed in the beaker set beneath the funnel. The basin with the platinum spatula in it, is once more placed on the water-bath for the second evaporation.

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[1] Lenher and Truog, Jour. Am. Chem. Soc., **38**, p. 1059, 1916.

While the second evaporation is in progress, the washing of the hr main portion of silica with cold, slightly acid water is completed. The filtrate is received in the 400-c.c. beaker previously used. The portions of wash-water added each time should be small, so as to keep down the volume of the filtrate.

When the second evaporation is complete and the salts are reduced to dryness and free from hydrochloric acid, occasional stirring with the spatula hastening the process, the mass is again moistened with a little hydrochloric acid (1 to 2 c.c.), and, after standing (warm) for five minutes, about 25 c.c. of water is added, and the whole is gently heated to complete solution (except for particles of silica).

The liquid is then filtered through a separate 7-cm. filter, the basin is well rinsed, and the filtrate and washings are caught in the 400-c.c. beaker that contains the previous filtrate. The small amount of silica is to be brought into the filter, and the basin is rubbed with a small piece of moist filter paper to remove adherent silica, and this is placed in the 7-cm. filter. Little washing is needed for this portion.

When washing is complete, the bulk of liquid, including all the washings in the 400-c.c. beaker, should not be more than 200 c.c., if the operation has been conducted with care and the amount of wash-water has been kept down.

Igition of Silica.—A *platinum*[1] crucible of 30- or 35-c.c. capacity is selected, preferably the latter if the rock contains much alumina or iron. This crucible is ignited, cooled in the desiccator and weighed. P179 The second filter, which contains the extra silica from the second evaporation, is removed from the funnel with the platinum spatula, placed in the crucible, heated until the paper is carbonized, and then reduced to ash. This will take but ten minutes or so.

When the crucible is cold, the free edges of the first filter, which contains the main portion of silica, are folded down on the silica so as to enclose it completely, the platinum spatula being used. The little package is then transferred with the spatula to the crucible, placed above the ashes in it, and preferably with the side uppermost that has three thicknesses of paper. The package is very gently worked and pressed down toward the bottom of the crucible, but the paper should not be torn, nor should all egress for steam from below be shut off. With a small piece of filter paper any particles of silica adhering to the spatula are rubbed off, and also any which may be on the funnel above the edge of the filter, and this piece of paper is also placed in the crucible. In this way the silica can be dried in the crucible and ignited, with no danger of loss from whirling up of the light powder.

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[1] A palau crucible should not be used for this ignition, because this is much more attacked than platinum in the subsequent pyrosulphate fusion. For the use of a fused silica crucible see page 178.

The *covered* crucible (vertical) is first heated at about 15 cm. above a low flame, the heating being cautious so as to avoid boiling of the pasty mass, and probable loss of substance or spattering of it on the sides of the crucible. This is continued until the contents are dry and the filter begins to char. As the water is driven off the crucible is gradually lowered, but this must be done with great caution, and the flame kept small. A filter that is carbonized at a low temperature is more easily incinerated than one that is carbonized rapidly and at a high temperature. The dried filter paper must not be allowed to burst into flame. The crucible is finally lowered close to the flame and heated until no more smoke is given off. The escaping vapors should never be allowed to ignite, and consequently the flame should be kept low and the bottom of the crucible should not be brought to a red heat until carbonization is complete.

The flame is then raised and the crucible is heated to a bright-red, being *vertical* and with the cover very slightly moved to one side, to allow entrance of some air, but not enough to give rise to dangerous drafts. *The flame must not envelop the crucible*, as an oxidizing atmosphere within it is essential and the light silica is easily carried off by drafts.

It is important to remember that the carbon must be entirely consumed over the Bunsen burner, so that the silica is perfectly white, as the subsequent prolonged heating over the Meker burner may not wholly oxidize any carbon that darkens the silica. The cover should be examined for adhering carbon, and if this is present it should be burned off by holding the cover in the flame.

When the carbon is entirely consumed and the silica is perfectly white, the cover is put in place, and a Meker burner is substituted for the Bunsen burner. The crucible is heated over it to a bright red for at least thirty minutes. This is necessary to effect complete dehydration of the silica, the last portions of water being retained with great tenacity. It also has the advantage of rendering the silica non-hygroscopic. The crucible is to be reheated to constant weight. The final result of the weighing is recorded as Cruc. + SiO_2 + x, above the weight of the empty crucible and also on the same line to the right.

Impurities in the Silica.[1]—The silica as thus obtained is never pure. It contains small quantities of Al_2O_3, Fe_2O_3, TiO_2, P_2O_5, and possibly other impurities, which may amount to one-half of one per cent or more in "basic" rocks. The correction of silica for these *must not be omitted* on any account, whatever be the kind of rock or silicate.

After weighing, therefore, the silica is moistened with 1 or 2 c.c. of water. In doing this the tip of the wash-bottle should be filled with water by blowing before inserting it in the crucible, to avoid blowing out any of the very light silica by the first puff of air from an empty tip. The stream is directed against the side of the crucible, the tip being inserted beneath the slightly raised cover.

Two drops of dilute (1:1) sulphuric acid are then added, this being necessary to retain the TiO_2, some of which would be vaporized as titanium fluoride in the absence of sulphuric acid. Hydrofluoric acid is then added, a few drops at a time. The action is apt to be violent, but with care and sufficient moistening of the silica no loss need be incurred. The hydrofluoric acid should be added in quantity sufficient to dissolve all the silica on warming. For this purpose 5, or at most 10 c.c. should be ample.

The crucible is then placed in a platinum triangle resting on a nickel crucible,[2] the wire of the triangle being bent and opened out so that the platinum crucible is well within it, but with the *sides not touching*. Or one may use a radiator, such as that described and figured by Hillebrand,[3] although the author always uses a nickel crucible. This arrangement insures uniform heating of the liquid and, with care, prevents "creeping" or loss by spattering.

The radiator and crucible within it are heated over a moderately low flame, so that the liquid does not boil, until the contents are nearly dry. Toward the end, when only a few drops of sulphuric acid are left, the operation may be hastened by cautiously heating the bottom of the naked platinum crucible with a small flame waved beneath it until all the acid is driven off. The whole of this operation must be conducted under a hood that is provided with a good draft.

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[1] Hillebrand, Bull. **700**, p. 103; Hillebrand-Lundell, p. 724; Mellor, p. 169; Treadwell-Hall, p. 416.

[2] A porcelain or low-form vitreosil crucible may be used if one of nickel is not at hand; but the evaporation is not as rapid.

[3] Hillebrand, Bull. **700**, p. 33; Hillebrand-Lundell, p. 21.

The crucible is then ignited over a Meker burner at a bright-red heat,[1] for at least fifteen minutes, to insure the decomposition of the sulphates of alumina, iron, and titanium and the complete expulsion of all traces of sulphuric acid. After it has cooled in the desiccator the crucible is weighed, and its weight is noted as Cruc. + x below that of Cruc. + SiO_2 + x, to the right. The loss in weight is that of the silica, to which is added later the small weight that is recovered from the pyrosulphate fusion (p. 182), before the percentage of SiO_2 can be correctly calculated.

The weight of this "silica residue" varies with the composition of the rock. In granites and other such acid or very salic rocks it is only a few milligrams, but it is greater with more basic rocks, up to about 0.5 per cent. If the rock is high in TiO_2 and Fe_2O_3 its amount is from 0.5 to 1.0 per cent, and occasionally more.

As was pointed out by Hillebrand, the composition of this residue is variable.[2] It always contains titania and ferric oxides, generally in largest amount, with alumina and a little phosphorus pentoxide. Aurousseau [2] found little lime in the residue from an andesite, but Beger [2] found much in that from a lamprophyre, as did Bloor [2] in that from a clay. There should be no SO_3 if the residue has been properly ignited. Only a portion of the TiO_2, of the rock is ever present, and the frequent assumption that the residue consists almost entirely of TiO_2 is *wholly unwarranted.* Investigation of the silica residue from different kinds of rock is highly desirable, as Aurousseau suggests.

The filtrate from the silica contains a little platinum chloride,[3] derived from the platinum basin during the evaporation for silica, and a little from the action of the hydrochloric acid on the manganate, if alcohol has not been added (p. 154). It is not necessary to remove this platinum before precipitation either with ammonia or sodium acetate. Correction for it will be discussed on page 182.

After having been weighed, the crucible (*uncleaned*) containing the residue from the silica is to be laid aside in a desiccator or other safe place, for use in the subsequent ignition of the precipitate of alumina, etc. (p. 177).

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[1] Blasting is not necessary.

[2] Cf. Hillebrand, Bull. **700**, p. 104; Hillebrand–Lundell, p. 725; Mellor, p. 170; W. R. Bloor, Jour. Am. Chem. Soc., **29**, p. 1603, 1907, (clay); M. Aurousseau, Jour. Washington Acad. Sci., **13**, p. 330, 1923; B. J. Beger, *Neu. Jahrb.*, Beil.-Bd. (A), **57**, p. 237, 1928.

[3] Cf. Hillebrand, Bull. **700**, p. 105, Hillebrand–Lundell, p. 729.

If a ‘‘vitreosil’’ crucible is used for the pyrosulphate fusion of the ammonia precipitate, (p. 178) the residue from the silica is to be brought into solution by adding a small lump (about 1 gram) of potassium pyrosulphate and carrying out the pyrosulphate fusion exactly as with the main ammonia precipitate. This is quickly carried out, and the cake in the crucible is laid aside to be dissolved and added later to the main portion.

‘‘**Soluble Silica.**’’[1]—In the examination of igneous rocks there may be occasion to determine the so-called ‘‘soluble silica,’’ that is to say, the silica separated in ‘‘gelatinous’’ or ‘‘granular’’ form on treatment of silicate minerals with acids. Before the days of the microscope this was very often done, but is now little used, except as a check on micrometric measurements of the thin section. The method depends on the solubility of such forms of silica, either ‘‘gelatinous’’ or ‘‘granular,’’ in alkaline solutions, and it is affected by the solubility of quartz in caustic alkali solutions. This, however, becomes serious only with extremely fine powders. Sodium carbonate solution is preferred by many to sodium hydroxide. As the method is rather crude at best, this is of little consequence.

To determine the ‘‘soluble silica,’’ one gram of the rock powder, of the usual degree of fineness, is evaporated to dryness in a platinum basin (large or small) with 25 c.c. of dilute hydrochloric acid, (1: 5). The dry (but not strongly heated) residue is moistened with the concentrated acid, diluted, boiled for a few minutes, and filtered. The residue, washed from the filter paper into a platinum basin,[2] is digested for fifteen minutes on the water-bath, and about 50 c.c. of 5 or 10 per cent sodium hydroxide solution (Hillebrand, Bull. 700, p. 245; Hillebrand-Lundell, p. 715), or a similar amount of sodium carbonate solution is added. It is filtered and the residue washed a few times with warm alkali solution. The filtrate is acidified with hydrochloric acid, evaporated to dryness, and the silica (now insoluble) is collected, well washed in the filter, ignited, and weighed, as in the main determination of silica. It is scarcely necessary, but is usually best, to correct this silica by evaporation with hydrofluoric acid.

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[1] Hillebrand, Bull. **700**, p. 244; Hillebrand–Lundell, p. 719; Treadwell–Hall, p. 433, Mellor, p. 668. Cf. H. S. Washington, Jour. Am. Ceram. Soc., **1**, p. 407, 1918.

[2] A porcelain basin may be used, but platinum is far better.

7. AMMONIA PRECIPITATE, (ALUMINA, ETC.)[1]

The filtrate from the silica contains the aluminum, iron, manganese, titanium, calcium, magnesium, barium, strontium, zirconium, rare earths, chromium, vanadium, and phosphorus of the rock, as well as a trace of silica that is still in solution, with large amounts of chloride of sodium derived from the carbonate fusion and that belonging to the rock, and of potassium from the rock. Of these, all are to be precipitated with the *alumina,* except the calcium, magnesium, barium, and strontium, and the sodium and potassium, and possibly except most of the manganese. It is no wonder that the student does not appreciate the complexities of rock analysis by learning how to analyze a feldspar, as is often the only practice that is given him in the analysis of silicates.

The best and most usually adopted method of effecting this separation is precipitation by ammonia, in the presence of sufficient ammonium chloride. An alternative method is a first precipitation by sodium acetate, but for general purposes this is much inferior to the other.

Errors in Alumina.—Of all the determinations of the chemical constituents of rocks, that of alumina is the most liable to error, not only in magnitude but in variety. This is due in part to its amphoteric character; in part to the gel-like consistence of its hydroxide, and consequent tendency to adsorption of salts and difficulty in washing, as well as its liability to pass through the filter; in part to the tendency of magnesia to be precipitated with it; in large part to the present necessity of determining alumina by difference, as no method is yet known for the satisfactory complete separation of alumina from all the other constituents and its direct determination, so that errors committed elsewhere fall on it; and in part to other causes.

The correct determination of alumina is, undoubtedly, more troublesome and difficult than that of any of the other chief constituents of rocks, and errors incidental to it have rendered unsatisfactory many otherwise fairly good analyses.[2]

Especial care must therefore be taken in all the manipulations and precautions that are involved in the determination of the various other constituents that are weighed with it. On the whole, the tendency is toward a plus error in the determination of alumina.

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[1] Hillebrand, Bull. **700,** pp. 106–115; Hillebrand–Lundell, pp. 69–70, 77–79; 393–398; 729–740; Mellor, pp. 177–184; Treadwell–Hall, pp. 422–423.

[2] Cf. H. S. Washington, Prof. Paper **99,** pp. 14, 17; also Hillebrand, Bull. **700,** p. 106; Hillebrand–Lundell, pp. 395–397.

Although the remarks above and the following list of errors may appear formidable and tend to discouragement, yet they should not be so regarded. To the careless or slovenly analyst the accurate determination of alumina is indeed beset with pitfalls; but if the proper precautions are observed the operation may be carried out with almost as much accuracy as that of the other constituents, in spite of its inevitable tediousness.

If ammonium salts are not present in sufficient amount some magnesia is precipitated with the alumina, thus increasing the apparent amount of the alumina and diminishing by just so much that of the magnesia. This is a very frequent error among the earlier analyses, and is committed too often at the present day. It is especially liable to occur with rocks that are high in magnesia, and should be carefully guarded against by the analyst; the more so, as this error is very easy to prevent. The analyst must therefore be sure that there is an abundance of ammonium salts, preferably the chloride, in the liquid. The presence of such salts also prevents the formation of colloidal solutions and the consequent ''running through'' the filter of the aluminum and iron hydroxides.

The first precipitate, whether by ammonia or sodium acetate, *must always be dissolved and reprecipitated,* even if the rock contains but little magnesia. This double precipitation is necessary because of the tendency shown by the gelatinous precipitate to adsorb dissolved salts, so that the first precipitate is invariably contaminated with salts of calcium, magnesium, and the alkali metals. If the rock is high in magnesia, a second or even a third, reprecipitation will be necessary to remove this entirely.

If the ammonia used is not fresh and contains ammonium carbonate, calcium carbonate will be thrown down with the alumina, and will, of course, increase the apparent weight of alumina and diminish that of the lime to the same extent. The ammonia should therefore, before using, be tested with calcium or barium chloride, and if a precipitate forms, the ammonia should be rejected, or boiled for a few minutes.

If ammonia is kept in a glass bottle, this is sure to be acted on by the alkaline liquid, rendering the ammonia impure, sometimes even to the extent of showing flakes of silica or partially decomposed glass. Such ammonia is not uncommon in many laboratories, but it should be unhesitatingly rejected as totally unfit for use, even after filtration.

In very accurate work the ammonia precipitation should be carried out in vessels of platinum or gold.

If crystalline salts are not present the colloidal hydroxides of aluminum and iron (especially the former) tend to pass through the filter. This tendency is less noticeable during the transfer of the precipitate to the filter than during the washing. It can be prevented by adding ammonium chloride or ammonium nitrate to the wash-water, which should be hot.

Prolonged boiling or standing after the addition of ammonia is to be avoided, as it tends to make the precipitate slimy and hard to filter and gives more opportunity for precipitation of lime by the atmospheric carbon dioxide. On prolonged boiling, furthermore, the ammonium chloride present may dissociate, leading to re-solution of some alumina by the hydrochloric acid set free, unless the liquid is sufficiently ammoniacal. On the other hand, ammonia in large excess may, and probably will, dissolve some aluminum hydroxide which will pass into the filtrate.[1] It was formerly recommended[2] that the precipitate should be washed entirely free from chlorides, because of the possibility of loss of alumina and ferric chlorides by volatilization. As regards aluminum, however, it has been shown[3] that there is no such loss, nor is there such loss of iron if the amount of ammonium chloride in the precipitate does not exceed about one per cent, which in analytical practice it never should.[4]

If the basic acetate method is used for the first precipitation there is a strong probability that some of the alumina and ferric oxide will not be precipitated and will pass through the filter. This can be avoided if the conditions as to the amount of free acetic acid are accurately adjusted; therefore care and strict attention should be paid to the suggestions made in the description of the method.

But even under favorable conditions, and in the hands of experienced analysts, a little alumina is likely to be found in the filtrate when the basic acetate method is used and even if ammonia alone is used, particularly with rocks that are high in alumina and low in iron. This alumina should always be recovered before precipitation of the manganous oxide, although this precaution is frequently neglected. The magnitude of the error for MnO is usually not very great, but may reach as much as two per cent of the rock, judging from some analyses with such abnormally, and otherwise inexplicably, high percentages of manganous oxide.[1]

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[1] Cf. Stieglitz, **1**, p. 196.

[2] Second edition, p. 101.

[3] Hillebrand, Bull. **700**, p. 108, note 3; Hillebrand–Lundell, p. 394; W. Blum, Jour. Amer. Chem. Soc., **38**, p. 1294, 1916.

[4] W. Daudt, Jour. Ind. Eng. Chem., **7**, p. 847, 1915.

The basic acetate method should therefore not be used by the inexperienced analyst, and unless the use of it is made advisable by the presence of much manganous oxide, it is best avoided altogether in rock analysis. In any case it should be carried out with the greatest care. Nearly all the authorities[2] emphasize the difficulties of the method and even advise against its use.

Another source of error that may affect the alumina determination is the incomplete reduction of ferric to ferrous iron for the determination of the total iron oxides (p. 183). The unreduced ferric oxide does not affect the permanganate and hence appears as alumina.

Some observations in the author's laboratory in the course of several analyses of rocks indicate that the weight of Al_2O_3 is too high by about 2.5 mg. for 1 gram of rock, chiefly due to the platinum taken up from the basin during the evaporations to render silica insoluble, and retained by the ammonia precipitate (p. 188).

The method of separation of alumina from ferric oxide by fusion of the ignited precipitate with sodium hydroxide in a silver crucible, which is sometimes recommended, should never be used. It is open to very grave objections and it offers no sufficiently compensating advantages.[3]

+ **Precipitation by Ammonia.**[4]—To the filtrate from the silica in the 400-c.c. beaker, which should amount to about 250 c.c., there is added 10 c.c. of concentrated hydrochloric acid.[5] The object of this is to form ammonium chloride on the addition of ammonia, in sufficiently large quantity to prevent precipitation of magnesia with the alumina and iron. Solid ammonium chloride is not to be used instead of ammonia and hydrochloric acid. One should avoid a large excess of ammonium chloride, so that for rocks such as granites and trachytes, which contain but little magnesia, the addition of 5 c.c. of hydrochloric acid will be sufficient. If the rock is very rich in magnesia 15 c.c. will not be too much.

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[1] Cf. H. S. Washington, Prof. Paper **99**, pp. 17, 20, 21.

[2] Fresenius–Cohn, **1**, p. 647; Classen, **1**, p. 465; Hillebrand, Bull. **700**, p. 109–Hillebrand–Lundell, pp. 342, 731; Jannasch, p. 319; Mellor, pp. 177, 362; Treadwell–Hall, p. 154.

[3] Cf. Hillebrand, Bul.. **700**, p. 132.

[4] Classen, **1**, p. 562; Fresenius–Cohn, **1**, pp. 623–625; Hillebrand, Bull. **700**, pp. 106–109; Hillebrand–Lundell, pp. 69, 393–398, 729–732; Mellor, pp. 177–183; Treadwell–Hall, pp. 422–423; H. W. Daudt, Jour. Ind. Eng. Chem., **7**, p. 847, 1915; W. Blum, Jour. Am. Chem. Soc., **38**, pp. 1282–1297, 1916.

[5] Addition of nitric acid is not necessary, as the ferrous iron will have been changed to ferric in the sodium carbonate fusion and in the evaporation. Nor is separation of platinum necessary, as recommended by Treadwell; on the contrary, its separation at this stage would be disadvantageous.

Before beginning the precipitation of alumina the analyst must decide whether to precipitate the whole of the manganese with it. The author's usual practice is not to precipitate the manganese here, because its amount is very small, seldom over 0.20 per cent, and this is distributed among the Al_2O_3, CaO, and MgO (p. 250), so that it may be disregarded. Lundell and Knowles[1] found that after two precipitations with ammonia less than 0.1 mg. of Mn_3O_4 was carried down with the alumina when 10 mg. of MnO was present. The MnO in the MgO and CaO can be determined colorimetrically. "It is recognized fully," as Hillebrand says, "that there are objections to parts of the procedure, but the same may be said of any other that is well known." The procedure adopted here is the simplest, and appears to be the most generally useful and sufficiently accurate for all but the most exigent work.

In accurate work, however, it is well to coprecipitate the manganese with the alumina. This would be especially advisable if the rock is low in silica or if the color of the carbonate melt shows that much manganese is present. The manganese thus affects the alumina alone and the weight of the ignited precipitate is then to be corrected for the manganese, as Mn_3O_4, determined later colorimetrically.

Several reagents will effect the quantitative precipitation of manganese with alumina. For many years the author has used ammonium persulphate for this purpose, and the same has also been done in the laboratory of the U. S. Geological Survey.[2] The addition of a sulphate is objectionable, chiefly because lime (and baria) are apt to be coprecipitated with the alumina. Mellor (p. 180) states that the precipitation of manganese by ammonia is incomplete in the presence of sulphates, but Hillebrand-Lundell (p. 394) state that "this has no basis in fact." Therefore it may be accepted that this particular objection to ammonium persulphate does not hold good. The other, however, does.

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[1] Lundell and Knowles, Jour. Am. Chem. Soc., **45**, pp. 676–681, 1923; Hillebrand, Bull. **700**, p. 108; Hillebrand–Lundell, p. 741.

[2] Hillebrand, Bull. **700**, p. 111; Hillebrand–Lundell, p. 731.

The matter has been recently investigated by Holt and Harwood,[1] who studied the effects of various oxidizing agents, including ammonium persulphate, hydrogen peroxide, chlorine, and bromine, as applied to the analysis of igneous rocks. They found that the first was objectionable because it was impossible to get all the calcium into the filtrate and because of the rather large amount of sulphate introduced. Hydrogen peroxide, which would seem to be the most satisfactory reagent, is objectionable because the precipitate invariably contains calcium, although the precipitation of manganese is quantitative, and the same is true of chlorine. Bromine was finally decided on as the best, and it is therefore recommended here to replace persulphate.

The liquid is colored with a few drops of methyl red,[2] and Blum's method of procedure[3] will be followed, except for the addition of bromine water. Concentrated ammonia is slowly added almost to precipitation[4] and the liquid is heated *almost to boiling,* when the Al_2O_3 is precipitated with a *slight excess of ammonia.* About 25 c.c. of saturated bromine water[5] is added drop by drop, the liquid being kept alkaline by the simultaneous addition of ammonia. Manganese will be precipitated as peroxide, while nickel and chromium remain in solution, the former as an ammonium double salt and the latter as chromate.

If ammonium persulphate is used instead of bromine, the procedure is much the same.[6] Ammonia is added to the liquid colored by methyl red until the indicator turns yellow. Then one gram of specially pure ammonia persulphate (p. 58) is added and then more ammonia, as described above.

The end precipitation, whether bromine is used or not, is done very slowly and cautiously, dilute ammonia water being used and added drop by drop, with constant stirring, until the color of the liquid changes to a distinct yellow. If much ferric hydroxide is present, which may mask the color of the liquid, the precipitate is allowed to settle a bit and if the liquid is still red dilute ammonia water is added as before to change it to yellow The liquid is then boiled for one or two minutes, *not more,*[1] and it must be distinctly yellow and smell but *faintly* of ammonia.[2] This careful procedure insures the complete precipitation of alumina and the other constituents with it, and at the same time prevents solution of alumina by an excess of ammonia.

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[1] Holt and Harwood, Mineral. Mag., **21,** p. 318, 1928.

[2] According to Blum, methyl red is the best indicator for this precipitation.

[3] Blum, *op. cit.,* p. 1295.

[4] This is to prevent effervescence and spattering on the addition of strong ammonia to a hot, very acid liquid.

[5] Holt and Harwood state that 15 c.c. of saturated bromine water is required if 10 mg. of MnO is present, and 40 c.c. if 50 mg. of MnO is present. A few drops of bromine may be used instead, as suggested by Mellor.

[6] Hillebrand–Lundell, p. 732.

The character of the ammonia precipitate differs much with the relative content in aluminum and ferric hydroxides. One that is very high in alumina is light colored and somewhat slimy, does not flocculate readily, filters and washes slowly, and tends to pass through the filter. That containing much iron is dark brown, flocculates more readily, is more easily filtered and washed, and does not tend to run through the filter. The greater the content of iron the darker the color.

After boiling, the liquid is *allowed to cool only until the beaker can be handled.* It is then filtered, *still hot,* through an 11-cm. filter[3] placed in a 7½-cm. funnel, the filtrate being received in a 600-c.c. beaker, unless the filtrate has been evaporated, as has been mentioned above, when a 400-c.c. beaker is used. This size of filter is appropriate for most rocks, but if the amount of $Al_2O_3 + Fe_2O_3$ is more than 30 per cent, one should use a 12½-cm. filter.

It is not necessary to take special precautions against the precipitate passing into the filter, though the greater bulk of the liquid can generally be transferred with but little of the precipitate doing so. Several washings by decantation, as are recommended by some, are not only unnecessary but are disadvantageous, as they will add much to the volume of the filtrate.

Because of its "salting" action in preventing the passage of the alumina through the filter it is best to add an ammonium salt to the wash-water. Ammonium nitrate is objectionable because, as was pointed out by Hillebrand, the platinum of the basin is liable to be attacked by chlorine during the subsequent evaporation. It is best to use ammonium chloride, which Blum has shown not to lead to loss of aluminum by volatilization of the chloride. One should therefore use for all the washings a hot 2 per cent solution of ammonium chloride, as recommended by Blum (p. 1290), or add a few drops of a strong solution of this to the filter during each washing.

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[1] Prolonged boiling is apt to give rise to the troubles mentioned on p. 103 and, besides, is quite unnecessary. The liquid is apt to bump badly and must be carefully watched. The old method of removing most of the excess ammonia by boiling has many objections and should be obsolete.

[2] If the liquid turns red on boiling, more dilute ammonia is to be added as before.

[3] An 11-cm. filter will hold the amount of ammonia precipitate corresponding to about 30 per cent of $Al_2O_3 + Fe_2O_3$ in one gram of rock. No. 589, black ribbon, is best; No. 590 is too thin and is apt to tear.

The beaker is rinsed out only two or three times with hot water,[1] which also serves to wash the precipitate in the filter. The beaker is not to be washed clean at this stage. The stream from the wash-bottle should break up the precipitate more or less, but *great care* should be taken not to throw too hard or sudden a jet directly onto the precipitate, which might easily throw some of it out of the funnel. Complete washing is not necessary at this stage, but about one-half centimeter around the edge should be washed clean, and the precipitate should be collected at the lower part of the filter.

In filtering and washing the ammonia precipitate it is very important that the mass be *not allowed to become dry.* This will not only form cracks that allow the wash-water to run through without removing soluble salts, but the mass will become hard and difficult or impossible to break up without danger of loss. The transfer of the liquid and precipitate to the filter and the washings should, on this account, not be interrupted. This is the filtration, above all others, *to which attention must be paid throughout*, and the analyst will soon realize the gain in time and satisfaction in results that come from observance of this precaution.

The filtrate from the ammonia precipitate almost invariably contains a little alumina, and possibly iron hydroxide, which are to be recovered as follows:[2] The filtrate and washings from the first precipitation are evaporated to small bulk, 50 to 100 c.c. This is best done in the platinum basin, and the liquid is to be kept alkaline by adding a few drops of ammonia from time to time.[3] The precipitated hydroxides are separated by filtering through a small filter. These, with those recovered similarly from the later washings, are to be ignited in the crucible that contains the silica residue (p. 163).

The first ammonia precipitate invariably contains magnesia, as well as some lime and alkali chlorides, so that its solution and reprecipitation at least once are necessary in all cases.

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[1] The water needed for the washing is to be kept hot in the hot-water wash-bottle, on the steam-bath, or over a low Bunsen flame, and not allowed to boil.

[2] Hillebrand, Bull. **700**, p. 113; Hillebrand–Lundell, p. 773; Mellor, p. 183.

[3] This evaporation may be proceeding while the main precipitation is attended to.

With the platinum spatula a side of the filter is loosened and a channel is made between the filter and funnel, so that all the liquid in the Piccard-tube and tubular part of the funnel may run out into the beaker below. The uncleaned stirring-rod remains in the 400-c.c. beaker and this is placed conveniently near the edge of the table. The funnel is removed from the stand, and with the platinum spatula the filter is gently loosened all around, the edge being turned down as little as possible, and the paper not being torn. The funnel is then held with its lower side horizontal and the folded part of the filter *underneath*, the spatula is slipped beneath this, and the filter with its contents are carefully removed from the funnel, and placed on the rear inside wall of the 400-c.c. beaker, held sloping in the left hand. The upper edge of the filter should be near the rim of the beaker. The filter is now unfolded,[1] opened out and gently spread and pressed against the glass, and this should be accomplished without tearing the paper. A little practice is necessary to accomplish this successfully.[2]

The main mass of the precipitate is pushed down to the bottom of the beaker with the spatula, which is washed off with a jet of water. The precipitate adhering to the filter is washed down and 50 c.c. of water is poured in. Twenty or so c.c. of hydrochloric acid[3] diluted to 1 : 1 or 1 : 2 are poured over the filter to dissolve any adhering precipitate, but without letting the paper slide down. The precipitate adhering to the sides of the beaker is also dissolved. The liquid is now brought to a volume of 100 c.c. or more. The liquid is heated until all the precipitate is dissolved, a drop of methyl red added, brought almost to a boil, and reprecipitated with ammonia, as before.

One or two c.c. of the macerated paper cream (p. 62) is added, and the paper well mixed with the precipitate by stirring. It should not be added before precipitation because some of the precipitate is formed in the fiber and tends to fireproof it, as pointed out by Hillebrand-Lundell. If there is to be a second reprecipitation, the paper pulp should be added then, not at the first reprecipitation. The addition of macerated paper was first suggested by Dittrich,[4] and its use is very advantageous in the *final* precipitation of gelatinous precipitates. The object of the addition is to distribute fibers of cellulose through the mass of the precipitate, so that on ignition the oxides will be loose and porous, not as a hard lump, thus permitting the more ready oxidation of any reduced ferric oxide, and also greatly hastening the subsequent solution in fused pyrosulphate. Experiments by Dr. H. S. Roberts and by the author show that there is no reduction of the ferric oxide if the procedure is properly carried out.

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[1] This is more difficult with the second method of folding the filter (p. 106).

[2] A filter-paper thus spread out is shown in the frontispiece, in the center.

[3] Nitric acid, which was formerly recommended, should not be used, because of the formation of chlorine, which will attack the platinum basin in the subsequent evaporation of the filtrate.

[4] Dittrich, pp. 10, 11, 14; Ber., **37**, p. 1840, 1904. Cf. Hillebrand–Lundell, p. 90; Mellor, p. 179.

With the paper still adhering to the rear wall of the beaker,[1] the contents, kept well stirred, are now passed through a fresh 11-cm. filter, placed in the funnel previously used, the filtrate being received in another 600-c.c. beaker.

If the rock contains much magnesia or lime, as with diorites, gabbros, basalts, tephrites, and peridotites, a second solution in hydrochloric acid and reprecipitation must be made, this being carried out exactly as before. The second filter is laid over the first.[1] Macerated paper may now be added. In this third precipitation the washing need not be as thorough as the first. A third precipitation is only called for if the rock is exceptionally high in magnesia, or in lime if the persulphate has been used.

After the final precipitation, whether it is the second or third, as much of the precipitate as is easily possible is to be transferred directly onto the filter. The sides of the beaker are washed down with strong jets of hot water containing 2 per cent of ammonium chloride, which is used for the whole washing. The adhering precipitate is loosened from the filters spread out on the rear wall of the beaker, but without disturbing them. The washings, in small portions at a time, with the precipitate that they carry, are poured into the filter.

In order to remove the last portions of precipitate, which cling tenaciously to the walls of the beaker, the filter paper hitherto spread on the rear wall is used as a swab. The lower third of this paper, that part which is most covered with precipitate, is moistened with water and torn off with the end of the stirring-rod, and is rubbed over the sides of the beaker. It is then, along with the loosened precipitate, washed into the filter. Another piece is then torn off and used in the same way, the lower part of the stirring-rod being cleaned by rubbing it against the mass of moist paper in the lip of the beaker. Four or five such rubbings will serve to use up all the previous filters, all portions of which must be brought into the funnel with the precipitate, and thus the interior of the beaker is rendered perfectly clean. The end of the rod is finally cleaned with a bit of moist filter paper which is added to the rest. The sides of the beaker are finally rinsed down all around with a small jet of hot water, and are examined to see if all the precipitate is removed.

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[1] Care should be taken to expel with the aid of the rod any liquid caught behind the lower part of the filter-paper on the rear of the beaker, and to mix it with the main portion.

[2] This second solution and reprecipitation is always advisable, except with such rocks as granite, rhyolite, and trachyte, that contain little magnesia.

The contents of the filter are then washed with many, (ten or twelve will usually suffice), portions of hot water, during which the mass is gradually brought down and collected in the lower part of the filter and the upper zone of this is cleaned of precipitate. This collection of the precipitate in the bottom of the filter and the cleaning of one-quarter or one-half a centimeter around the edge is practically important, as it greatly facilitates the subsequent transfer to the crucible for ignition.

For ordinary work, in a third precipitation only the rinsings and first washings need be caught in the beaker, as the amount of magnesia or lime in the final washings would be inappreciable, and these washings would add considerably to the volume of the liquid for lime and magnesia.

The combined filtrates from these washings are to be evaporated down as before (p. 172), to recover any hydroxides of aluminum and iron. Inasmuch as by this time there is much ammonium chloride present, it is best to carry this evaporation to dryness, and expel the ammonium salt by gentle heating. As the mass of salts is apt to decrepitate and lead to loss, the method of J. Lawrence Smith may well be used. It is thus described by Hillebrand-Lundell (p. 119): Render the solution slightly acid with hydrochloric acid, concentrate it in a suitable beaker or large porcelain basin, and then add approximately 3 grams of nitric acid for every gram of ammonium chloride. An excess does no harm, and 25 or 30 c.c. will usually be sufficient. Cover the beaker, warm gently until the vigorous evolution of gas ceases, and then evaporate to dryness.

The final combined filtrates from the ammonia precipitate, which may amount to about 250 c.c., are reserved in a covered 600-c.c. beaker for the determination of lime and magnesia (pp. 201, 205).

Omit **Basic Acetate Precipitation.**[1]—The difficulties, uncertainties, and dangers of this method have already been pointed out (pp. 14, 167); and once more it is strongly urged that it be not used, except in unusual cases, where the ordinary and simpler method of precipitation by ammonia will not serve. It is described here, very reluctantly, partly because it may rarely happen to be the best method available, especially when much manganese is present, and because, being a method often recommended, the description may aid the student to avoid some of its pitfalls. The basic acetate method is, of course, *absolutely unnecessary* if the manganese has been precipitated with the alumina by bromine or persulphate.

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[1] Classen, **1**, 465; Fresenius–Cohn, **1**, p. 647; Hillebrand, Bull. **700**, pp. 109–110; Hillebrand–Lundell, pp. 71, 731; Mellor, p. 362; Treadwell–Hall, p. 153.

To the cold filtrate from the silica, in the 400-c.c. beaker, the volume of which is about 200 c.c., and contains a little free acid, a strong solution of sodium carbonate is added cautiously until the fluid turns a dark red and a slight turbidity is observed, that does not disappear on stirring. This addition is to be made in the beaker covered with a watchglass, and the solution of carbonate is introduced through the small funnel with bent tip, to avoid loss by effervescence. The watchglass, the tip of the funnel, and the sides of the beaker are rinsed down, and if these rinsings are sufficiently acid to redissolve the slight precipitate, as may sometimes happen, a few more drops of carbonate solution are added until a slight permanent precipitate is again formed.

Dilute hydrochloric acid is then added, drop by drop and very cautiously, with constant stirring, until the slight precipitate and turbidity *just* disappear, the fluid still retaining its deep-red color. Especial caution is needed here, as any decided excess will set free enough acetic acid to render incomplete the precipitation of basic acetates of alumina and iron. If too much has been added, therefore, the solution is again to be slightly more than neutralized with sodium carbonate and treated with dilute hydrochloric acid more cautiously.

About two grams of sodium acetate dissolved in a little water are then added. This is the amount for most rocks, but it may be varied somewhat with advantage. Thus for rocks low in the sesquioxides, as granites and rhyolites, one gram may serve, though two will not be amiss. But in such rocks as nephelite-syenite, phonolite, gabbro, basalt, or tephrite, which contain large amounts of these oxides, the quantity would best be increased to three grams, which may be considered the limit.

If the liquid has not a volume of 300 c.c., it is diluted to this bulk, or to 350 c.c. if the larger amount of sodium acetate has been used. It is heated to boiling and allowed to boil for not more than a minute, because prolonged boiling renders the precipitate slimy and difficult to filter. After settling for a few minutes, the liquid is filtered through an 11-cm. filter, and washed only two or three times with hot water. This precipitate, which consists of basic acetates of aluminum and iron, with the titanium, zirconium, chromium, and phosphorus of the rock, is rather *more apt to run through the filter* than the precipitate of hydroxides produced by ammonia. The washing, therefore, should not be thorough, and it is as well to add a little sodium acetate to the hot wash-water, so as to have a crystalline salt present.

After this slight washing the precipitate is dissolved in hydrochloric acid by the method just described, *reprecipitated with ammonia, not with sodium acetate,* and this solution and reprecipitation by ammonia is repeated if the rock demands it, exactly as was done in the method by ammonia alone. The final precipitate is to be ignited as described below. As before, the final filtrate is reserved for the dermination of lime and magnesia (pp. 201, 205).

The filtrates from the sodium acetate and from the ammonia precipitates are to be evaporated down separately and treated as described on p. 172 for the recovery of the hydoxides of aluminum and iron. These will be usually appreciably larger than when ammonia alone is used. It is best to carry the evaporation of the first to dryness, to expel acetic acid, but it should not be heated over the flame. If manganese hydroxide is deposited on the dish, it is to be dissolved in a little dilute hydrochloric acid with a drop or two of sulphurous acid or a sulphite.

Ignition of the Precipitate.[1]—The moist final precipitate in the filter is allowed to drain well and, if time permits, is advantageously kept for half an hour or so, the funnel covered with a filter paper, so as to dry it out somewhat. It is then placed moist in the crucible that has been used for the determination of silica, and in which there still remains the residue left on evaporation with hydrofluoric acid (p. 164).

The transfer is done with the aid of the platinum spatula, the free edges of the filter being folded over inward, the filter is very gently freed from the funnel without tearing the paper, and the whole is carefully placed in the crucible with the three-fold portion uppermost. Care should be taken not to soil the sides of the crucible, and to leave abundant free passage for the exit of steam from beneath the mass. The spatula and interior of the funnel are to be cleaned with a small piece of filter paper, which is laid on top of the package in the crucible.

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[1] Hillebrand, Bull. **700,** p. 114; Hillebrand–Lundell, pp. 397, 734; Mellor, p. 183.

A 30-c.c. crucible of fused silica or "vitreosil" may be used instead of one of platinum for the pyrosulphate fusion. This has the advantage of enabling one to watch the fusion through the sides of the crucible and so guard against the rising of the molten mass. The melt is also not contaminated with platinum, so that a correction of the alumina for this is not necessary. Incidentally the cake detaches itself much more readily from fused silica than from platinum. For this purpose a transparent crucible is much better than one of translucent silica, both because it is more easily seen through and because the former kind is of better quality than the latter.

On the other hand, for this fusion a silica crucible has the serious objection that some silica may be taken up from it and so be added to the small amount of silica in the ammonia precipitate. For this reason Hillebrand-Lundell (p. 705) say justly that a fused silica ("quartz") crucible should not be used for the pyrosulphate fusion. This objection is valid, especially in very accurate work, when a platinum crucible must be used. But tests made in the author's laboratory show that the loss in weight of a "vitreosil" crucible is only 0.02 to 0.04 gram for an ordinary fusion, so that the weight of "extra" SiO_2 would be negligible for most purposes.

It must be noted that if a fused silica crucible is used for the pyrosulphate fusion the residue from the silica (p. 164) must be fused with a small amount of pyrosulphate and the solution of the cake is to be added to the main portion.

The drying of the moist mass must be done *very cautiously*, at a height of about eight inches or so above the low flame, the crucible being *vertical and covered.* Constant attention and patience are necessary to prevent any bubbling of the pasty mass, which would soil the upper portion of the crucible with precipitate and render difficult its complete solution in fused pyrosulphate. The crucible is very gently and cautiously lowered as the mass dries off, until the filter is carbonized, when it is heated vertically for a short time at a bright-red heat until the cover is free from adhering carbon.

The crucible is then laid sloping on its side on the platinum triangle, the mouth at the twisted end, and the cover is leaned against it, almost vertical, with its upper edge a little below the top of the crucible, leaving a narrow opening above and below. This is done to ensure an oxidizing atmosphere within the crucible during the ignition.

The flame is then directed against the bottom and lower third of the crucible, the flame not being violent enough to cause dangerous drafts, and the incineration of the paper is soon accomplished. It is then heated at a bright-red over a Meker burner for at least 30 minutes. This will insure complete incineration of the filter and the reoxidation of any ferrous oxide that may have been formed, which will be much easier and more complete if macerated paper has been added during the final precipitation. As the last portions of water are said not to be always completely expelled by the heat of a Bunsen or Meker burner, the crucible may be blasted for 10 minutes.[1] The author has found, however, that blasting is not necessary, and that prolonged heating to constant weight over a Meker burner is sufficient. During this heating the crucible should be vertical and covered, and the flame playing only on the bottom of the crucible.

After the crucible has been cooled in the desiccator it is weighed,[2] and should then be reheated over the Meker burner to constant weight. The difference between this weight, recorded as Cruc. + Al_2O_3, etc. and that of the empty crucible obtained prior to the ignition of the silica (p. 160), is that of the Al_4O_3, with the total iron as Fe_2O_3, TiO_2, P_2O_5, Mn_3O_4,[3] ZrO_2, the rare earths, Cr_2O_3, V_2O_3, and a trace of silica. The amounts of these various constituents that accompany the alumina are determined separately, and that of Al_2O_3 by difference. If three 11-cm. filters or one of 12½ have been used the weight of their ash is to be subtracted from that of the ignited precipitate.

The ignited precipitate in the crucible is used for the determination of the total iron, titania, and the trace of silica, its solution being effected by fusion with potassium pyrosulphate. This process may best be begun immediately after weighing the precipitate, as it takes several hours.

Fusion with Pyrosulphate.[4]—The ignited ammonia precipitate is very complex. It contains, with all rocks, all of the alumina, total iron oxides as ferric oxide, titania, phosphorus pentoxide, and manganous oxide (as M_3O_4) if bromine or persulphate was added before the precipitation, as well as the small amount of silica that has escaped the first evaporation to dryness. With some rocks it also contains all of the chromium, vanadium, zirconia, and the rare earths. All of these constituents except the trace of silica are determined in separate portions and duly allowed for in order to arrive at the weight of the alumina.

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[1] Blum (Jour. Am. Chem. Soc., **38**, p. 1293, 1916) has shown that blasting for 10 minutes is as effective as for half an hour.

[2] Blum (*op. cit.*, p. 1292) has shown that alumina is markedly hydroscopic, even if blasted, so that it is advisable to keep the crucible closely covered during the weighing, which should be done as rapidly as possible. Cf. Hillebrand–Lundell, p. 396.

[3] If manganese has been precipitated by bromine or by ammonium persulphate.

[4] Mellor, p. 184; Hillebrand, Bull. **700**, p. 116; Hillebrand–Lundell, p. 736. Hillebrand adopts a somewhat different method. He points out that solution in

The precipitate is best brought into solution by fusion with potassium pyrosulphate, which operation is carried out as follows:[1]

Five to seven grams of potassium pyrosulphate[2] in lumps or coarse powder are placed in the crucible containing the precipitate, so as to completely cover this, great care being taken to avoid mechanical loss of the precipitate. The amount used will vary somewhat with each rock, but those mentioned will usually be sufficient. In general, it is hardly necessary to weigh out the pyrosulphate, but enough should be added to fill the crucible about one-third when fused.

The crucible is placed over a low flame and *heated gently until the salt is fused.* It is then raised to a distance above the flame (about 20 to 30 cm.), where the pyrosulphate will remain in a state of fusion and the moisture that it contains will be driven off, *without any boiling or spattering* against the crucible cover. With some practice the height can be easily adjusted. This point is an important one to attend to, because any drops on the cover or the upper sides tend to spread on further heating and run over the edges, leading to loss of iron. The whole process at this stage must be carefully watched to guard against this mishap.

It may happen, even if great care is taken, that there is a slight creep of the salt around the rim and about the cover. This is usually due to carelessness and is almost always caused by too intense or too rapid heating. This deposit should not be touched when moving the crucible to the stone slab or disturbed during the cooling.

In the course of half an hour or so all the moisture will be driven

hydrochloric acid, recommended by earlier writers, is not effective. Furthermore, the iron should be in solution as a sulphate for proper titration with permanganate. Cf. Treadwell–Hall, p. 100; Kolthoff–Furman, Vol. Anal., **2,** p. 309.

[1] Precipitates with much iron are more readily soluble in molten pyrosulphate than are those high in alumina, and the liquid is much darker.

[2] It is important that the pyrosulphate must be fused and anhydrous. The crystallized bisulphate spatters badly and is apt to froth.

off, and the crucible can be lowered gradually until it is immediately above the small flame, where it is kept in fusion for another hour or more. Here also the contents should be watched at short intervals to see that there is no spattering. The precipitate will have been gradually dissolving and the fused salt becomes darker in color. The larger lumps of oxide stay at the bottom, while small particles may float on the top of the liquid.

When the greater part of the floating portion has dissolved, any small particles that may be adhering to the sides above the level of the liquid may be washed down by a slight rotary motion of the crucible. This more intense heating should be carried out with caution to avoid boiling, and, until the last stages, the bottom of the crucible should not be allowed to become red-hot. White vapors of sulphur trioxide are given off, and the crucible is examined every now and then until all of the floating precipitate has been dissolved. If any particles obstinately adhere above the liquid, the crucible may be held obliquely in the triangle, to let the fused salt act on these.

The heat is then increased somewhat until the bottom of the crucible is a faint red, the liquid becoming thicker through loss of sulphur trioxide and the formation of the more difficultly fusible normal potassium sulphate. The liquid mass also becomes dark brown, almost opaque if much iron is present, the depth of color increasing with the temperature.

The bottom of the crucible may be examined, notwithstanding the darkness of the liquid, to see if all the precipitate has been dissolved, by removing the flame and allowing the crucible to cool with the cover off. The fused mass will gradually become less opaque and lighter in color, until it is transparent enough to be seen through[1] before solidification begins at the surface, unless there is much Fe_2O_3. — Couldn't see through; turned light then col

When no more undissolved substance is visible, the heating at a low red heat is continued for half an hour, to render complete solution certain, and the crucible is placed on a stone or iron slab to cool.[2] The cake loosens far more readily than that of the sodium carbonate fusion, often with a ringing sound, and it also cracks, so that its removal is not difficult.

This operation calls for almost constant attention and it takes much time. In reality, however, after one has had a little practice in adusting the heat at the various stages, only an occasional glance is necessary, and the whole can often be accomplished in three or four hours, especially if macerated paper has been used, so that the oxides are in the form of a powder. This, moreover, is of no great importance, as the analyst can attend to other parts of the analysis.

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[1] This is more easy with potassium than with sodium pyrosulphate. The examination should be made near a window or below a light.

[2] The platinum Blair crucible tongs (p. 38) should be used for this, or the crucible be moved held between the bowed portion of the ordinary tongs.

When the mass is thoroughly cold the crucible is placed on its side in a 250-c.c. beaker. The under side of the cover is also washed into this crucible to remove any spattered drops of pyrosulphate, with possibly the application of a drop or two of dilute sulphuric acid. If there are many drops, or if they persist, the cover is also placed in the beaker.

If it is desirable to apply the correction for platinum the washed crucible (and cover) should be ignited and weighed once more, so as to ascertain the loss in weight after the pyrosulphate fusion.

The final volume of liquid in the beaker may be about 100 c.c., to which about 3 c.c. of concentrated sulphuric acid is added. This not only facilitates solution of the pyrosulphate but prevents reversion to or precipitation of metatitanic acid, which would diminish the apparent amount of titania determined later by the colorimetric method. The beaker (covered) is then heated over a low flame or on the water-bath until solution is complete, except for traces of silica which are practically insoluble in the melted potassium pyrosulphate. heated 3 hrs not would go into soln —

Hr.

The contents of the beaker are filtered through a 7-cm. filter into a 300-c.c. Erlenmeyer flask, the beaker being rinsed half a dozen times, and the rinsings passed through the filter. The volume of filtrate should not be more than 150 c.c. If the fusion has been successful a few flakes of silica only will remain on the filter. If not, there may be present some small, dark particles of undissolved oxide.

In either case the filter is placed in an *unweighed*, small platinum crucible, carbonized at a gentle heat, strongly ignited, and weighed. A drop of dilute sulphuric acid and two or three drops of hydrofluoric acid are added, driven off by gentle heating, and the crucible is again ignited and weighed. The loss in weight represents the trace of silica, which is to be added to that of the main portion, already determined (p. 163). It will seldom amount to more than a milligram. not

The residue left in the crucible, which contains a little iron and titanium oxides, is dissolved by fusion with a small lump of potassium pyrosulphate, which is quickly effected. After cooling, this is dissolved in the crucible with a little warm water containing a drop of sulphuric acid, and the solution is poured into that in the 300-c.c. flask, the crucible being rinsed into this. to hr.

8. Total Iron Oxides[1]

The solution of the pyrosulphate fusion, obtained as above, is used for the determination of the total iron oxides as ferric oxide and for that of titania. For the former the ferric sulphate is reduced to ferrous salt and titrated with permanganate; for the latter a colorimetric method is almost invariably used.

Errors.—The most frequent and most serious error involved in the iron determination is incomplete reduction of the ferric oxide. This can be guarded against by allowing the hydrogen sulphide to pass for a longer time than that which experience has shown to be generally necessary and by not boiling down to a very small bulk. This error should be guarded against by testing the solution for the presence of ferric iron when reduction is assumed to be complete.

A second source of error is the deterioration in the titer of the permanganate solution, which can be avoided by keeping it under proper conditions and frequently restandardizing it (p. 63). These precautions are often not sufficiently observed.

With proper precautions, errors involved during the titration, such as oxidation by atmospheric oxygen, are negligible.

If hydrogen sulphide is used as a reducing agent, and the reduction is carried out as described below, the results are "reasonably accurate," but Lundell and Knowles find that, as usually performed, reduction by hydrogen sulphide and titration with permanganate give slightly high results, probably due to the formation of polythionates.

Reduction of Ferric to Ferrous Iron.—The filtered solution of the mixed sulphates contains all of the iron in the ferric state. This must be reduced to the ferrous for titration with potassium permanganate to determine the total iron oxides.

Several reagents may be used for this reduction. The best are hydrogen sulphide and sulphur dioxide; metallic zinc has also been used.[2]

Although zinc is often recommended, as by Mellor (p. 187), the

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[1] Classen, **1**, pp. 454–455; Gooch, pp. 141–146; Hillebrand, Bull. **700**, pp. 119–121; Hillebrand-Lundell, pp. 304, 738; Mellor, pp. 451–453; Treadwell-Hall, pp. 99–100; Lundell and Knowles, Jour. Amer. Chem. Soc., **43**, p. 1560, 1921; Kolthoff–Furman, Vol. Anal., **2**, pp. 308–314.

[2] Kolthoff–Furman, Vol. Anal., **2**, pp. 312–316.

$$Fe_2O_3 + H_2S \longrightarrow 2FeO + H_2O + S$$

author is most strongly opposed to it for rock analysis. The chief and decisive reason is that zinc reduces titanic sulphate to the titanous salt, which is oxidized by permanganate and hence will appear as ferrous oxide.[1] As titanium is present in all igneous rocks, this is a fatal objection to the use of zinc in the analysis of rocks.[2]

Sulphur dioxide is an excellent reducing agent, as it does not reduce quadrivalent titanium. But it reduces platinum to the bivalent condition, and as platinum is present in the filtrate from the pyrosulphate melt in the analysis of rocks, this metal must be removed (as by H_2S) and the iron oxidized before the final reduction by SO_2.[3] Hillebrand and Lundell and Knowles speak well of it, except for its action on platinum, but it is not favored by Kolthoff-Furman, who state that it takes a long time to remove the excess. The author much prefers H_2S. If SO_2 is used it is most conveniently obtained from a cylinder of the gas. A solution of SO_2 on standing develops oxidizable substances; and sulphites also are not stable and develop thionates, etc., if they are not fresh. These salts, therefore, should not be used, although Mellor (p. 187) advocates ammonium bisulphite.

Hydrogen sulphide has the great advantage of not reducing quadrivalent titanium and easy and complete expulsion. Although it precipitates platinum, this, as will be seen, is rather an advantage than a disadvantage. It is, therefore, to be used, as the reducing agent for ferric iron in rock analysis; this has been done by the U. S. Geological Survey for many years. The present method for the reduction of ferric to ferrous iron by hydrogen sulphide differs in certain minor details from that described in previous editions of this book, in conformity with the recommendations of Lundell and Knowles,[4] with some modifications, chiefly because of the presence of platinum.

A current of hydrogen sulphide,[5] washed with water in the usual manner, is passed at the rate of a bubble a second, through the solution in the 300-c.c. Erlenmeyer flask,[1] the gas being introduced through a bent glass tube reaching to the bottom of the flask. The liquid should be at room temperature, with the acidity from 1.5 to 2.5 per cent of H_2SO_4 by volume. The gas is bubbled for thirty minutes through the acid solution, and then for fifteen minutes through the solution as it is raised to boiling. It is then allowed to cool, with the gas still passing.

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[1] Vanadic sulphate is also reduced by zinc, but this of slight importance.

[2] If zinc is used for the reduction, which is or should be complete for the titanium, titania must be determined and allowance made for its effect: the same amount of permanganate is used to oxidize Ti_2O_3 to TiO_2 as to oxidize FeO to Fe_2O_3.

[3] Cf. Lundell and Knowles, *op. cit.*, p. 1567; also Hillebrand, Bull. **700,** p. 186; Hillebrand–Lundell, p. 303.

[4] Lundell and Knowles, Jour. Am. Chem. Soc., **43,** p. 1565, 1921; Hillebrand–Lundell, p. 304. The present author still advocates the use of H_2S, despite the criticisms of Hillebrand–Lundell.

[5] This operation must be done under a hood, with a good draft.

The solution gradually becomes dark and turbid, but on boiling the liquid becomes clear and the separated sulphur coagulates. This is colored black or dark brown by the presence of platinum sulphide derived from the platinum basin and crucibles, and with palladium or gold sulphide if a palau basin has been used.

The current of hydrogen sulphide is cut off, and the glass tube is rinsed, inside and out, into the flask. The contents are filtered through a 7-cm. filter into a 500-c.c. Erlenmeyer flask and the filter and sulphides are well washed with cold water containing some hydrogen sulphide.[2] This filtration and washing may be done outside the hood, and the operation is to be carried out as quickly as possible and the filter should be kept full. Six or eight rinsings of the flask and passage through the filter should be sufficient. Because of the presence of finely divided sulphur the filtrate almost always becomes opalescent, but this is of no consequence, as it is oxidized by the sulphuric acid present in the subsequent boiling.[3] The filter containing the sulphur, dark with platinum, is to be kept for determining this (p. 188). It is well to remove it from the funnel while still moist.

About 15 c.c. of dilute (1:1) sulphuric acid is added. The solution of the small cake from the trace of silica (p. 182) is poured in, if it has not been added before, and the crucible is washed once or twice, the excess of hydrogen sulphide present being more than sufficient for complete reduction of the ferric sulphate that it contains.

It will now be best to test the liquid to ascertain if reduction is complete.[4] This is done by taking out a drop on the end of a stirring-rod and adding it to a few drops of potassium sulphocyanate solution in a watchglass resting on a white porcelain plate. If a red color appears, hydrogen sulphide should be passed through the liquid in the 500-c.c. flask for another fifteen minutes. It will not be necessary to filter after this, as the precipitated sulphur has no action on permanganate.

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[1] The volume may be from 150 to 200 c.c., although Lundell and Knowles recommend that it be 100 c.c.

[2] This is prepared in a 150-c.c. beaker (under the hood) after the reduction is finished.

[3] In any case, such sulphur (free from platinum) has no effect on permanganate, as shown by Lundell and Knowles.

[4] Connor (C. R. XIII Cong. Geol. Int., p. 886, 1914) suggests nearly neutralizing the liquid before passing H_2S, thereby obtaining complete reduction. R. S. McBride concludes from his experiments that the acid concentration should range from 1.5

Three or four small pieces of platinum foil, bent at right angles, are then dropped in, to prevent bumping on boiling.

The volume of the filtrate, by now, may be 250 c.c. The flask is placed over a flame, and a carbon dioxide generator is set in action, the gas being freed from possible hydrogen sulphide (due to sulphides in the marble) by passing through a column of copper sulphate solution and then through water. The carbon dioxide is allowed to bubble through at the rate of about two bubbles per second, and is passed into the liquid through another piece of bent glass tubing.[1] Complete saturation of hydrogen sulphide is indicated by small bubbles of this gas which rise in the liquid soon after the heating begins, and long before it has become hot enough to simmer or boil.

The flow of carbon dioxide is kept up after boiling has begun, and the boiling is continued briskly for thirty minutes, when the expulsion of hydrogen sulphide should be complete. This is shown by testing the issuing steam with filter paper which has been dipped in lead acetate solution.

There is no danger of reoxidation of the ferrous sulphate, since at first the liquid contains hydrogen sulphide, and later the boiling is carried out in an atmosphere of steam and carbon dioxide.

The boiling off should not be carried so far as to diminish the liquid to less than one-half of its original volume, as hot, strong sulphuric acid solution has an oxidizing effect on ferrous salts. The final volume may be about 200 c.c.

The flame is now extinguished, and the hot flask is grasped by the neck with a towel. While the stream of carbon dioxide is still passing into the flask, the hot flask is placed in a capacious vessel, such as a basin, or a large, deep, thick-walled trough or crystallizing dish (p. 40), that is set near at hand. This contains water, but to a depth not above that of the solution in the flask. Some cracked ice is added, the ice-water not rising above the level of the liquid in the

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to 2.5 per cent of H_2SO_4 by volume for complete reduction. (Hillebrand, Bull. **700**, p. 120.

[1] The end of this may be drawn out to a capillary so that the gas bubbles will be small and numerous.

flask, and care being taken that the flask does not tip over. The stream of carbon dioxide is continued during the cooling.

Titration of Iron.[1]—The stock-bottle of permanganate solution is gently shaken, to wash down any drops of water that may have distilled onto the upper part of the bottle, and the solution is poured through a small funnel into a weight-burette with stop-cock closed, which is held in place in the clamp on the clamp-stand.

If the rock is known to contain but little iron, as with a granite, a trachyte, or a rhyolite, a 50-c.c. burette will answer; otherwise one of 100 c.c. is to be taken, and this is always safer. In either case the burette is to be almost full.[2]

The burette is then weighed, but *only to the nearest centigram,* as this corresponds to one-hundredth of one cubic centimeter, less than can be measured on a Mohr's burette, and so is exact enough (cf. p. 123). The burette is again placed in the clamp and raised to a height that will just permit the Erlenmeyer flask to be slipped beneath its tip. The cap that guards the tip is removed, and the stopper is turned so that the small perforation in it and the one in the neck coincide.

If an ordinary Mohr's burette is used, it is made ready as usual, the meniscus being brought to the zero-line.

When the contents are cold, the flask is placed on a white porcelain plate,[3] or a sheet of white paper, its mouth just below the tip of the burette, and the permanganate is dropped slowly into the liquid, not running down the sides of the flask. The flask is given a rotary motion with the left hand, to distribute the permanganate and lessen the chance of splashing. If any drops fall or are splashed on the sides of the neck they are washed down into the flask with cold, boiled water. With a little practice the proper manipulation is easily learned and the titration quickly carried out.

When the amount of standard solution needed is roughly known, about half of this may be added quickly in portions of one or two cubic centimeters at a time, with rotary motion of the flask to disappearance of the color after each addition. When the color begins to disappear slowly, single drops are to be added with great caution, until one drop produces throughout the liquid a pink blush which does not vanish on stirring or rotating for a short time. As very dilute solutions of permanganate are unstable, this color will vanish on long standing, even when the reaction is complete. After waiting a few moments after the addition of the last drop, the burette is wiped off and again weighed.

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[1] For a description of the operation of titration, see p. 121.

[2] The author's 50-c.c. burette, filled with permanganate solution, weighs about 125 grams, that of 100 c.c. about 180 grams.

[3] In moving the flask the hand may be placed over its mouth to keep the carbon dioxide atmosphere in it. The gas inlet tube may be left in or, if removed, is slightly washed off both inside and outside, the washings falling into the flask.

The ~~weight in grams~~ no. c.c. used of permanganate solution used is then multiplied by the amount of Fe_2O_3 equivalent to one ~~gram~~ c.c. of the standard,[1] the product giving the total iron in the rock determined as Fe_2O_3. From this is to be deducted later the iron present as FeO.

After titration of the iron, 2 or 3 c.c. of hydrogen peroxide are poured in. This colors the liquid yellow because of the titania, which is always present.[2] The contents of the flask are used for the determination of titania (p. 189). If a series of analyses is being made, the flask (covered with a small beaker) is to be set aside, as the colorimetric operation for TiO_2 is best made in several batches, to conserve the standard titanium solution.

Correction for Platinum.[3]—Platinum has been introduced into the analysis at several points. A little is derived from the crucible during the sodium carbonate fusion; more is derived from the basin during the evaporation of hydrochloric acid to dryness to render silica insoluble;[4] a third portion is added during the pyrosulphate fusion. It is not known definitely how these portions are distributed, but the author is inclined to think that the largest amount comes from the platinum basin, but the crucible during the pyrosulphate fusion adds almost as much, the amount from the sodium carbonate fusion being slight. The total weight of this platinum is small, but inspection of the progressive loss of weight suffered by the same platinum crucible after a long series of pyrosulphate fusions leads one to believe that it is, for each analysis, approximately 2.5 milligrams, or about 0.25 per cent of the rock, of which about one-half should be subtracted from the alumina.

In order to estimate the amount of this correction, the filter with its contents of sulphur and sulphides may be ignited in a small weighed porcelain crucible and the weight of the metallic platinum ascertained. From this weight is to be subtracted the loss in weight of the platinum crucible after the pyrosulphate fusion, the difference being the weight of platinum taken up from the basin during the evaporation of hydrochloric acid. This weight of platinum is to be subtracted from the weight of alumina before calculation of its percentage (p. 179). The application of so small a correction is uncalled for in ordinary work, and then only if the rock is high in iron. It is disregarded by Hillebrand[1] and almost always by the author.

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[1] If a Mohr's burette is used, cubic centimeters are to be understood here instead of grams.

[2] After a little experience one learns to estimate roughly the amount of TiO_2 in the rock from the depth of color.

[3] If a palau crucible or basin has been used palladium is taken up instead of platinum.

[4] This is greatest if the rock is high in iron.

9. TITANIA[2]

For the determination of titania the whole volume of the solution in which the total iron has been titrated is best adapted. This contains all of the titanium in solution as sulphate, and with no possible traces of hydrofluoric acid, which exerts a deleterious effect on the colorimetric method. If, for any reason, this solution is not available, the titania can be determined in a separate portion of rock powder, one gram of which is brought into solution with a mixture of dilute sulphuric (1:1) and hydrofluoric acid. This is continued until fumes of sulphuric acid are given off, but not to dryness, when more of the dilute sulphuric acid is added, and the evaporation is continued until there are no traces of hydrofluoric acid, which may take four or five repetitions and additions of sulphuric acid. Or the solution in which ferrous oxide has been determined will answer, if it is evaporated down (in platinum) repeatedly with sulphuric acid to completely expel the hydrofluoric acid.

There are two very different methods—colorimetric and gravimetric—by which titania is determined in rocks. The former is, by far, the most accurate and most expeditious, is best adapted to the small quantities of this constituent that are usually present in rocks, and is the method that is used by the chemists of the U. S. Geological Survey and in general by the author. It will therefore be described first, and in detail; the gravimetric methods will be taken up later because they are needed if the amount of titania is very high, and because all analysts may not have at hand the appliances necessary for the colorimetric determination.

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[1] Hillebrand, Bull. **700**, p. 105. Hillebrand-Lundell, p. 729.

[2] The author has adopted throughout the name *titania* instead of titanium dioxide, in order to be consistent with "zirconia," "strontia," etc. "Titania," therefore, is always to be understood as meaning titanium dioxide, TiO_2.

Volumetric methods for titania[1] will not be described here. They are lengthy and tedious, and are not adapted to the analysis of rocks, although they may serve for industrial work.

Colorimetric Method.[2]—This method, which was suggested by Weller, depends on the yellow coloration of titanium solutions produced by hydrogen peroxide, possibly, but doubtfully, through the formation of titanium trioxide,[3] the depth of color being proportional to the amount of TiO_2. Lenther and Crawford[4] suggest the use of thymol for the colorimetric determination of TiO_2; but the very great intensity of the color produced would seem to make this method inapplicable with many rocks.

Errors.—In the colorimetric method for titania there are few sources of serious error, though some corrections may have to be applied.

Vanadium, molybdenum, and chromium interfere, the first two because of the similar coloration of their solutions by hydrogen peroxide, and the last because of the normal color of the chromates. It is very seldom, however, that either of these elements is present in sufficiently large amount to seriously affect the determination.

Hillebrand[5] was the first to show that even very small amounts of hydrofluoric acid "render this method inexact by partly bleaching the yellow color." The hydrogen peroxide must therefore be free from fluorine, as must also be the solution in which the titania is determined. This bleaching effect, it may be added, has been utilized by Steiger and Merwin for the determination of fluorine (p. 266).

Solutions of ferric sulphate are yellowish, so that the color of this compound will be added to that of the titania treated with peroxide. In general, this error will be practically negligible, but it may be serious if the rock contains much iron, 10 per cent or more of the oxides.

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[1] Cf. Hillebrand, Bull. **700,** p. 166; Hillebrand–Lundell, pp. 459, 749; Kolthoff–Furman, Vol. Anal., p. 329.

[2] A. Weller, Zs. Anal. Chem., **23,** p. 410, 1884; Classen, **1,** pp. 776–778; Hillebrand, Bull. **700,** pp. 155–162; Hillebrand–Lundell, pp. 457–459, 747–749; Mellor, pp. 203–206; Treadwell–Hall, pp. 102–104; Thornton, Titanium, pp. 127–138; Yoe, Colorimetry, pp. 384–385.

[3] Cf. J. W. Mellor, Treatise Inorg. Chem., **7,** p. 63, 1927. Thornton (personal communication) thinks that this is improbable.

[4] Lenher and Crawford, Chem. News, **107,** p. 152, 1913; Jour. Am. Chem. Soc., **35,** p. 138, 1913; Cf. Scott, p. 444; Yoe, Colorimetry, p. 381.

[5] W. F. Hillebrand, Jour. Am. Chem. Soc., **17,** p. 718; 1895.

A correction for this disturbing effect of high iron may be made on the basis of Hillebrand's tests,[1] that "go to show that the coloring effect of 0.1 gram of Fe_2O_3 in 100 c.c. of 5 per cent sulphuric acid solution is about equal to 0.2 milligram of TiO_2 in 100 c.c. when oxidized by hydrogen peroxide. This amounts to a correction of only 0.02 per cent [of TiO_2] on 1 gram of rock containing the unusual amount of 10 per cent Fe_2O_3."

The error may also be corrected by adding to the standard solution a quantity of ferric sulphate in a weak, acid solution of known strength equal to that formed by the weight of ferric iron, which has been determined. Or the color of the ferric sulphate may be bleached by adding a small amount of phosphoric acid, the same amount being added to the standard solution after the peroxide has been dropped in and before being made up to a known volume. For most rocks, however, such corrections are hardly called for.

Merwin [2] has shown that alkali sulphates have a marked bleaching effect. As his standard was prepared free from alkali sulphate, there can be no doubt as to the reality of the effect. He shows, however, that the bleaching is diminished, and indeed rendered almost, if not wholly negligible, if sufficient sulphuric acid is present.

In regard to the correction for the effect of alkali sulphates we cannot do better than to quote Merwin (p. 122) verbatim.

"In rock analysis, by using 6 grams of pyrosulphate, which is equivalent to 4 grams of normal sulphate and 2 grams of acid, for the melt containing the titanium, and dissolving this in water to which 10 c.c. of strong sulphuric acid has been added, a nearly negligible correction of only 3 per cent (of the TiO_2) need be added. If the TiO_2 exceeds 0.02 gram no correction is required (as the color is so intense that the bleaching effect will not be noticeable). In case the melt is dissolved in 100 c.c. of 5 per cent sulphuric acid, the titanium found—if the amount is between 0.002 gram and 0.01 gram —is too low by approximately 0.0004 gram."

It will be seen that for most work the correction is negligible if the solution is made very strongly acid.

Dunnington [3] pointed out the necessity for the presence of at least 5 per cent of sulphuric acid, but his explanation that this prevents the formation of metatitanic acid, which does not become colored by hydrogen peroxide, is probably only partially correct, as was pointed out by Merwin, the solutions used by him not being strongly enough acid to prevent the bleaching effect of the alkali sulphate. The presence of at least 5, or better 10, per cent by volume of H_2SO_4 is necessary, also, to prevent hydrolysis of the titanium on standing.

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[1] Hillebrand, Bull. **700**, p. 160; Hillebrand-Lundell, p. 457; Thornton, Titanium, p. 134.

[2] H. E. Merwin, Am. Jour. Sci., **28**, p. 119, 1909.

[3] F. P. Dunnington, Jour. Am. Chem. Soc., **13**, p. 210, 1891.

Phosphoric acid has also a bleaching effect, but the amount of it in rocks is so small that this factor is negligible.

The eye must be practiced in color distinctions, and the illumination must not affect the color of the solution. For this reason the determination must not be made at night.

The Procedure.—The preparation of the standard solution containing 0.01 gram of TiO_2 in 10 c.c. has already been described (p. 68). It will be assumed that the Kober colorimeter or one of a similar type (p. 51) is used. The manipulation with other forms will be described later.

The whole volume of liquid used in the titration for total iron oxides serves for the determination of TiO_2. It will have been already rendered yellow by hydrogen peroxide, but if not, or if it has stood a long time, 1 c.c. of hydrogen peroxide is poured in. The depth of color indicates the amount of TiO_2. About 10 c.c. of concentrated sulphuric acid is also slowly added.

The volume to which the solution is diluted depends on the percentage of TiO_2. For most igneous rocks the volume is to be made up to 500 c.c.[1] by pouring the solution (when quite cold) into a 500-c.c. measuring-flask, the Erlenmeyer flask being rinsed out several ok times, the rinsings added, and the flask then filled to the mark.

If the yellow color is very light, as with most granites and rhyolites, which contain much less than one per cent of TiO_2, the liquid is to be evaporated down[2] to a bulk of 200 c.c. and, when cold, poured into a 250-c.c. measuring flask. A little hydrogen peroxide is added to restore the color, and the flask is filled to the mark. In a few cases (when the percentage of TiO_2 is less than 0.5) it may be necessary even to reduce the final volume to 100 c.c. On the other hand, if there is much TiO_2 say 4 to 6 per cent, the final volume may be 1000 c.c., but in such cases it is better to determine the titanium gravimetrically (p. 197).

The liquid in the measuring flask must be thoroughly mixed.

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[1] This volume is appropriate for rocks in which the percentage of TiO_2 is from 0.5 to 4.0.

[2] This is the best done in the platinum basin, though one of porcelain may be used.

This is done, not by shaking, but by inverting the closely stoppered flask several times, the stopper being held in place by the fingers, and the large air-bubble acting as a stirrer.

This final measured volume of liquid is known as the *test solution.* One soon learns to judge from the color as to about what the final volume of the liquid should be. The depth of color of the test solution should best be considerably different from that of the diluted *standard solution,* prepared as described below. In the example given later, and as is the author's usual practice, the test solution is considerably darker than that of the diluted standard. In accordance with the principle underlying the colorimetric method, with the Kober colorimeter and similar types the height of the column of liquid observed is inversely proportional to the TiO_2 (or MnO) content per cubic centimeter.

The delicacy of this or of any other colorimetric method[1] is greatest if the color is neither very deep nor extremely light;[2] therefore if much titanium is present the dilution should be great. The most favorable tint is a rather deep straw color, about that of light beer, or of clear, light amber. This corresponds almost exactly to Ridgway's "light cadmium."[3] Stated quantitatively, according to Wells "the accuracy of the comparison is practically constant for concentrations ranging from 1.5 to 20 mg. of TiO_2 in 100 c.c.," and a favorable concentration is one between 0.5 and 1.5 mg. TiO_2 in 10 c.c. Solutions containing more than 20 mg. TiO_2 in 10 c.c. are too deeply colored to be suitable and should be diluted.

The procedure is conducted as follows:[4] The colorimeter is placed in position facing a window, the instrument being vertical. The two mirrors are adjusted to give maximum illumination, and one should see that this is equal on both sides, slightly turning the eyepiece if necessary. The two cylindrical cells should be of opaque black glass, with clear, colorless bottom, which should be fused on.

One of the two cylindrical cells is partly filled with the standard solution, *S;* the other with the test solution, *T.* These are placed in position, the two shelves being lowered for this purpose. It is immaterial on which side these are placed, but it is well to adopt a uniform practice. Let us assume that T is on the right.

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[1] For discussion of the errors of colorimetric methods see Yoe, Colorimetry, pp. 83–90.

[2] See R. C. Wells, Jour. Am. Chem. Soc., **33**, p. 504, 1911, as to the sensitiveness of the colorimetric estimation of titanium. He estimates the accuracy of colorimetric comparisons to be about 2 per cent.

[3] R. Ridgway, Color Standards, Washington, 1912, Plate IV, 19.

[4] The description applies especially to the Kober colorimeter. The details of the procedure differ according to the type of instrument used; the general principles remain the same.

The glass T is now raised to a fixed point on the scale; let us say at 50. This also is optional, but it is essential that the end of the black glass tube of the colorimeter *dips into the liquid* and that the glass does not contain so much solution as to overflow. The point selected will also depend on the depth of color. The position must be exactly ascertained with the aid of the vernier. It is to be remembered that the color of the liquid in the *right-hand* glass appears on the *left* half in the eyepiece, and conversely, in the Kober instrument.

The glass S is now raised cautiously until the black tube dips into the liquid, avoiding any overflow, and is moved to about the same position as T, to note which is the darker. Let us assume this to be T, although it is immaterial. The glass S is then gently moved up and down until the color of S matches that of T. This is to be done several times, both by raising and lowering the glass. The position of S is then read with the vernier and noted. The glass S is then lowered (or raised) several divisions, so that the two shades are distinctly different, and the operation of matching is repeated. This should be done several times, and the average of three measurements is taken. With care and practice the variation of the several measurements from the mean should be small—certainly well within one small division of the scale.[1] If the difference is greater than this, the series is to be repeated, possibly changing the position of T.

The mean of the position of S is then divided by that of T, if T is the darker at equal heights, as the amount of TiO_2 per cubic centimeter varies inversely as the depth of liquid through which the light passes. If S is the darker at equal depth, the ratio $\frac{T}{S}$ is used. The former is the author's general practice, and it is as well to follow one or the other. But here, again, it is optional which is done.

The equation $\frac{S}{T} = n$ (or $\frac{T}{S} = n$) represents[2] the weight of TiO_2 per cubic centimeter of the diluted test solution if the standard contains exactly 0.001 gram TiO_2 per cubic centimeter. In this case

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[1] As an example, the readings may be 32.2; 32.7; and 32.3. The mean of this is 32.4.

[2] The figure for the darker is always the denominator.

100.5°

this value is multiplied by the whole number of cubic centimeters to which the test solution has been diluted, giving the total weight of TiO_2 in the rock. As, however, the standard titanium solution has seldom the exact content of 0.01 gram of TiO_2 per 10 c.c., or if on restandardization it is found that the concentration has changed, n must first be multiplied by the correct weight of TiO_2 per cubic centimeter before multiplying by the total volume of test solution. The percentage of TiO_2 in the rock is, of course, that of this weight divided by the weight of rock powder taken for analysis.

The operation must be carried out in the daytime, and best on a bright day, because the shades of color are much more readily distinguishable by daylight than by artificial light. It will be found advantageous to rest the eyes from time to time by looking at the floor or at a dark corner, as their sensitiveness is apt to diminish through fatigue.

To economize the standard solution, it is well to make TiO_2 determinations in several rocks at one time.

If the Kober or a similar type of colorimeter is not available, one may use the Weller colorimeter described by Hillebrand,[1] the making of which has been described on page 51 above. In this type the depth of color is directly proportional to the amount of TiO_2 per cubic centimeter and inversely proportional to the volume, as the lengths of column observed are the same. The previous detailed description of the operation with this colorimeter is repeated here in a condensed form.

An indeterminate quantity of the test solution is poured into one of the square colorimeter glasses, say the right-hand one. Then 10 c.c. of the standard titanium solution, containing about 0.01 gram of TiO_2 (the quantity being known) is removed from the stock-bottle with a dry 10-c.c. pipette and placed in a 10-c.c. measuring flask. A few cubic centimeters of hydrogen peroxide are added, and the liquid is diluted to the mark and well mixed.[1] Each cubic centimeter of this diluted standard will contain about 0.0001 gram of TiO_2. The color must be deeper than that of the test solution, so that 20 c.c. (instead of 10) of the standard may be diluted to 100 c.c.

Two Mohr's burettes are fixed in a stand; the one is filled to the mark with the diluted standard, the other with water, also filled exactly to the mark. Then 10 c.c. of the diluted standard is run into the left-hand glass, and water is added to this from the other burette in small portions at a time. After each addition the liquid is mixed by a gentle rotary motion, and the color is compared with that of the test solution. The shutter is slid down until only the liquid in each glass is visible, and the liquids are viewed against a window. As the color of the standard approaches that of the test solution the addition of water should be cautious and toward the end only by a few drops at a time, until the point of agreement is reached, when the amount of water used is read off and noted down. The liquid is rejected. Again 10 c.c. of the diluted standard is run into the empty left-hand glass, and water is added as before, the water burette being refilled if necessary. This procedure is repeated on a third portion, and the mean of the three additions of water is obtained. The three additions should not vary more than within 1 c.c.

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[1] Hillebrand, Bull. **700**, pp. 35–37; Hillebrand–Lundell, pp. 24–26.

[2] This volume will serve for the TiO_2 determinations in three rocks.

The principle underlying the simple calculation is that by adding a known volume of water to 10 c.c. of the diluted standard the final content in TiO_2 of each cubic centimeter is known. As the colors match and the length of the column observed is the same, this will be the TiO_2 content per cubic centimeter of the test solution. Thus the total TiO_2 is this amount multiplied by the volume of the diluted standard.

(used)

If the colorimeters described above are not available, Nessler tubes may be used. Two tubes are placed side by side in a light box, resting on a ground-glass plate forming a false bottom, or on a horizontal wooden partition with holes, or a broad slot cut so as to admit light from below. Beneath this or the ground-glass plate a mirror is fixed at an angle of 45° above the real bottom, admitting light from a side-opening and transmitting it vertically up through the tubes. It is simpler to hold both tubes side by side above white paper, with a darkened cardboard screen around them to cut off the side light.

The test solution is prepared as above, but the standard is used undiluted. One Nessler tube is filled with the colored test solution up to the 50-c.c. mark, and in the other is placed 5 c.c. of hydrogen peroxide, which is diluted with a known volume of water nearly up to the same mark. The standard solution is then added in very small quantities at a time from a burette, the liquid being stirred, and the colors observed after each addition, until there is agreement between the two. After a few trials, and with knowledge of the approximate amount of titanium present in the rock, the heights of the two solutions can be made sensibly identical, but several determinations are always advisable. The amount of TiO_2 in the known volume of

100cc containing .01 g
=.001

standard solution used is that of the TiO_2 in 50 c.c. of the test solution, and hence shows its TiO_2 content per cubic centimeter.

A better form is the Eggertz tube, or its Julian modification, in which the test solution is matched against the standard, diluted to a known amount. The comparison may be made, in diffused sunlight, by holding the two tubes side by side at an angle of 45° to a sheet of white paper with their lower ends touching it. The contents should be kept well mixed. In this case, as with the Kober type, the concentration of TiO_2 is inversely proportional to the heights of the columns.[1]

None of these simpler forms yields as accurate results as the more complex colorimeters, although they serve for rapid, industrial work. For accurate analysis the others are to be employed.

omit
201

Gravimetric Methods.[2]—Although the colorimetric method for the determination of titanium is by far the simplest and the most expeditious, is capable of great accuracy, and is applicable to the great majority of rocks, it is not well suited to rocks that contain more than about 4 per cent of TiO_2. This is chiefly because of the loss in delicacy with great depth of color, and because any error is magnified with great dilution. Occasion may therefore arise for the determination of titania by gravimetric methods, although these take much more time and are not recommended if the colorimetric method is applicable.

Gooch's Method.—A good gravimetric method is that of Gooch,[3] which has been considerably modified. We follow Thornton's description of the procedure. The method consists essentially in removing the iron as sulphide, the alumina and titania being held up by tartaric acid. After destruction of this, the titanium is precipitated and weighed as TiO_2.

Hillebrand has shown that zirconia prevents the complete precipitation of titanium by boiling in acetic acid solution. But this is of no practical importance because zirconium is never present in more than traces, if at all, in rocks that are high in titanium, where such traces would have no appreciable influence. On the other hand, rocks that (for this constituent) are high in zirconia contain very little titania, so that the colorimetric method will always serve with them. For these reasons the author is of the opinion that Hillebrand attaches far too much importance to this defect in the Gooch method, *as applied to rocks,* although the objection may be valid with certain silicate *minerals.*

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[1] Cf. Yoe, Colorimetry, pp. 13–14.

[2] Hillebrand, Bull. **700**, pp. 162–166; Hillebrand–Lundell, pp. 460–461, 749; Mellor, pp. 206–210; Treadwell–Hall, p. 160; Thornton, Titanium, pp. 95–98.

[3] F. A. Gooch, U. S. Geol. Survey, Bull. **27**, p. 16, 1886; Hillebrand, Bull. **700**, p. 162; Hillebrand–Lundell, p. 461; Treadwell–Hall, **2**, p. 160; Thornton, Titanium, pp. 95–98, 192.

The solution of the pyrosulphate cake after the determination of total iron oxides (p. 188) is evaporated down to a volume of 100 to 200 c.c.[1] according to the amount of iron present. Tartaric acid is added "in amount equal to three times the aggregate weight of the oxides to be held in solution," or three times that of the weight of the ignited alumina precipitate less the weight of the total iron oxides. This may be done by the addition of the solid acid or (best) as a strong solution. The liquid is made neutral with ammonia, and 2 or 3 c.c. of sulphuric acid (1:1) is added. Hydrogen sulphide is then passed through the cold liquid for at least twenty minutes, until the liquid becomes colorless and the iron is reduced to the ferrous state.[2] Ammonia is added to decided excess, more hydrogen sulphide is passed in for ten minutes or so, and the flask is allowed to stand until the ferrous sulphide settles. The ferrous sulphide is then filtered off into a 400-c.c. beaker, and is washed with water containing a little ammonium sulphide, made fresh by passing hydrogen sulphuric through slightly ammoniacal water, taking the precautions mentioned on page 185. The filtrate, which should be pale yellow[3] and perfectly clear, is strongly acidified with sulphuric acid and the hydrogen thus liberated and that in solution is expelled by boiling gently in the covered beaker for half an hour. It is best to test the liquid for hydrogen sulphide with lead acetate in a drop on a watchglass.

When the hydrogen sulphide has been completely expelled, the tartaric acid, which holds up the titanium, must be completely destroyed, unless cupferron is available. There are two usual methods of doing this:

1. A strong solution of potassium permanganate (made by dissolving in a little water permanganate crystals weighing two and one-half times the weight of tartaric acid used) is added *gradually* to the hot solution (the beaker being covered). Vigorous reaction ensues, with the formation of brown hydrated manganese peroxide. When the brown precipitate does not perceptibly dissolve in the

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[1] This is best contained in a 400-c c. Erlenmeyer flask.

[2] Titanium will come down with the iron sulphide unless all the iron is reduced.

[3] There is, of course, no methyl red present.

boiling solution, one may be sure that the tartaric acid has been oxidized as far as formic acid (which is all that is necessary). But it is well to continue to add permanganate until the solution is slightly colored by it. The liquid is allowed to cool and is decolorized by adding a few drops of a solution of ammonium bisulphite. Ammonia is added to the cold solution in slight excess, followed at once by acetic acid in considerable excess, and the titanium is precipitated as metatitanic acid by boiling for one minute. The precipitate is collected on a 7-cm. filter, washed with water containing both sulphurous and acetic acids, ignited in a platinum crucible, and weighed as TiO_2.

As this TiO_2 is generally contaminated with manganese, it is fused with one gram of sodium carbonate, and the cold cake is treated with 5 c.c. of sulphuric acid (1:1) in the covered crucible, the crucible being warmed cautiously when action ceases. The syrupy liquid, (which may be turbid), is poured into 100 c.c. of cold water, and the crucible and cover are well washed with this. To reprecipitate the titanium, ammonia is added in sufficient quantity to *just* precipitate the titanium, and the titanic acid is dissolved by adding enough dilute sulphuric acid (1:1) corresponding to 2.5 grams of pure acid. Acetic acid is added to make up about 10 per cent of the final volume in absolute acid (about 100 c.c. of the 30 per cent acid), and 20 grams of sodium acetate (dissolved in a little water) is stirred in. The solution, the volume of which should be about 400 c.c. (in a 600-c.c. beaker), is brought rapidly to a boil and the boiling is to be continued for *only one minute*. The precipitate is washed first with acetic acid of 7 per cent strength and then with hot water, ignited over a Bunsen burner and weighed as TiO_2.

2. Thornton[1] has proposed the use of *fuming* nitric acid to destroy the tartaric acid. Its chief advantage is that of not introducing substances that would contaminate the titanic acid, and thus making unnecessary a second precipitation in rocks and minerals with little Al_2O_3 and much TiO_2. For general purposes it would seem that the method with permanganate is to be preferred, but for details the student may consult the papers cited.

A modification of Gooch's method, due to Professor H. Fay, is described by Warren[2] and was inserted in the previous edition. It is omitted here because Gooch's or Thornton's method as described above is better, and still better is the use of cupferron.

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[1] W. M. Thornton, Jr., Am. Jour. Sci., **34**, p. 214, 1912; and Titanium, p. 98.

[2] C. H. Warren, Am. Jour. Sci., **25**, p. 23, 1908.

The ancient method of precipitating metatitanic acid by boiling a slightly acid solution of the sulphate in the presence of sulphur dioxide is not to be used. It is not reliable, has other defects, and has been abandoned by all good analysts.[1]

Cupferron Method.[2]—The use of cupferron, which does not precipitate alumina and phosphoric oxide, does away with the necessity of destroying the tartaric acid—a somewhat tedious and messy process.

The solution in which the total iron oxides have been determined is evaporated down to small bulk, tartaric acid is added, first made neutral with ammonia, followed by the addition of a little dilute sulphuric acid, and then treated with hydrogen sulphide to reduce the iron, which is precipitated by ammonia, exactly as has been described in the first part of the Gooch method.

To the filtrate from the iron sulphide is added 40 c.c. of dilute sulphuric acid (1:1) and the hydrogen sulphide is expelled by boiling and diluted to a volume of 400 c.c. We here quote Thornton's description of the procedure (Titanium, p. 90):

"The 600-c.c. beaker is placed in a bath of finely cracked ice, and a recently prepared and filtered 4 per cent solution of cupferron is added drop by drop with constant stirring till present in considerable excess. One and a half times the theoretical amount[3] will do no harm. The titanium comes down as a canary-yellow flocculent precipitate, which is easily coagulated by stirring and filters rapidly without the aid of suction. The supernatant liquid should be tested by adding a little more of the reagent. The formatoin of a small white precipitate of nitrosophenylhydroxylamine, which soon vanishes, indicates that the reagent has been added in excess, while a yellow turbidity shows that more is needed. It is well also to test the filtrate. The precipitate is collected on a paper filter,[4] set in a long-stem funnel and braced by a perforated platinum cone, and is washed twenty times with ice-cold dilute hydrochloric acid (1:9). After having been sucked dry from drainage liquid, the paper and precipitate are placed in a weighed platinum crucible and dried in the oven at 110°. The ignition is begun with a very small flame. After the first violent gush of smoke, the temperature is raised gradually until the carbon has been consumed, and then the full power of the Meker burner is applied for twenty minutes. The product is titanic oxide of definite composition.''

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[1] Hillebrand, Bull, **700**, p. 154; Mellor, p. 207; Thornton, Titanium, p. 91.

[2] Hillebrand, Bull. **700**, p. 165; Hillebrand–Lundell, pp. 110, 461, 749; Thornton, Titanium, pp. 90, 98.

[2] This would be 7.75 (say 8) times the weight of the TiO_2.

[4] A Gooch crucible cannot be used because of the liquefaction of the precipitate on heating.

We have found that suction is not necessary if the funnel with a Piccard tube (p. 41) is used, and that it is not necessary to support the filter on a platinum cone, although a small 5½-cm. filter may be used for this, or a double filter may be used. As Thornton says, the precipitate is ''prone to develop mud cracks and should therefore be agitated with the stream of water from the wash-bottle as much as possible.'' If 4 per cent or more of TiO_2 is present, two 12½-cm. filters should be used, as the precipitate is very bulky, the precipitate being distributed between the two. Great care and some attention are needed during the early part of the ignition, and *the flame is to be kept low.* The abundant carbon that is deposited on the crucible is easily burned away, but it should be seen that the cover is free from carbon.

Care should be taken that none of the cupferron solution gets on the hands, as phenylhydroxylamine solutions are active skin poisons.

Cupferron precipitates zirconium with the titanium, and the weight of the TiO_2 is to be corrected for that of the ZrO_2 which is determined in a separate portion, or in this portion as $TiO_2 + ZrO_2$.[1] But, as has been said above, this will seldom, if ever, be necessary, because titanium and zirconium are not present in large amount together in igneous rocks.

continue

10. LIME[2] (AND STRONTIA)

For the determination of lime, the filtrate from the ammonia precipitate is used (p. 175); ~~or if manganese has been determined as sulphide (p. 177),~~ the filtrate from this may be used, in which case the ammonium sulphide need not be driven off. The volume of liquid should not amount to more than about 400 c.c., and this is contained in a 600-c.c. beaker. If the volume is more, it is advisable to evaporate it down (in a porcelain, fused silica, or platinum basin) to 400 c.c. This should not be necessary if care has been taken to avoid unduly large quantities of wash-water or if the filtrate from the ammonia precipitate has been evaporated to recover aluminia.

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[1] J. Brown, Jour. Am. Chem. Soc., **39**, p. 2356, 1917.

[2] Classen, **1**, p. 794; Fresenius–Cohn, **1**, pp. 270–272; Gooch, pp. 86–88; Hillebrand, Bull. **700**, pp. 140–148; Hillebrand–Lundell, pp. 486–503, 744; Mellor, pp. 211–214; Treadwell–Hall, pp. 81–84.

The lime may be weighed as CaO after ignition of the oxalate, or the precipitate of this may be titrated volumetrically. The former is the method that is almost universally adopted, except for rapid, industrial work.

Errors.[1]—There are comparatively few errors involved in the determination of lime if the operations are properly carried out. Indeed, as has been said already, this constituent and silica are those that are most likely to be approximately correct in second-rate analyses.

The first precipitate of calcium oxalate invariably contains magnesia and soda, so that solution and reprecipitation *are always necessary*. The oxalate must always be ignited to constant weight, even when experience has taught one the time necessary for ignition. Blasting is not necessary.

The error caused by the presence of carbonate in the ammonia has been mentioned on p. 166, in connection with the determination of alumina. This, of course, would render the apparent amount of lime too low, but it can be prevented very easily by testing the ammonia with barium chloride. The magnitude of this error will never be very great, unless grossly impure or very old ammonia is used.

In rare cases the weight of the CaO is to be corrected for that of the SrO. There is no danger of barium contaminating the oxalate after two precipitations. For very accurate work the weight of Mn_3O_4 with the CaO may be estimated colorimetrically; but in most cases it is negligible.

Precipitation.—The filtrate from the ammonia precipitate that is used for the determination of lime should contain sufficient ammonium chloride to prevent any coprecipitation of magnesia. Therefore, if the ammonium chloride has been driven off (p. 175), about 10 c.c. of hydrochloric acid is added, the liquid is colored with methyl red, and rendered decidedly ammoniacal. It is heated almost to boiling, during which 1 to 3 grams of ammonium oxalate are dissolved in a little hot water. When the ammoniacal filtrate begins to boil, this solution of ammonium oxalate is added in small portions at a time, with constant stirring. The boiling is continued for a few minutes, and is laid aside for about four hours. If there is but little lime a longer time is advisable—overnight will do no harm.

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[1] Blasdale, pp. 214–215; Hillebrand, Bull. **700**, p. 140; Hillebrand–Lundell, pp. 493–497; Mellor, pp. 211–212; Treadwell–Hall, pp. 82, 86; Richards, McCaffrey, and Bisbee, Proc. Am. Ac. Arts and Sci., **36**, p. 375, and Zs. Anorg. Chem., **28**, p. 71, 1901.

The liquid is filtered through a 7- or 9-cm. filter, the filtration and first washing being carried out as described above (p. 104). The filtrate is received in an 800-c.c. beaker, and is reserved for the determination of magnesia (p. 205).

After slight washing, the precipitate in the filter is dissolved and washed into the original 600-c.c. beaker (as has been described on p. 108), about 1 c.c. of ammonium oxalate solution is added to the filtrate, the liquid is heated nearly to boiling, and the lime is reprecipitated by the slow addition of sufficient ammonia to give a strong ammoniacal odor.

I let stand 1 day

After standing from four to six hours[1] the precipitate is filtered off, the filtrate passing into a second 600-c.c. beaker. The calcium oxalate is well washed, but not over-washed, a drop of the ammonium oxalate solution being added with each addition of wash-water. A second reprecipitation is not called for.

The precipitate is ignited moist as already described (p. 118). The calcium oxide is ignited over a Meker burner for twenty minutes, which will be more than sufficient to completely change all the oxalate to oxide in most rocks. Blasting is quite uncalled for, and should not be used, because it may lead to the platinum being attacked by the lime, as pointed out by Hillebrand-Lundell (p. 500). The calcium oxide is to be kept covered in the desiccator, and weighed as rapidly as possible as soon as it is cold, the crucible being kept well covered. In all cases the oxide is to be reignited to constant weight. The final weight is divided by that of the rock powder taken, to arrive at the percentage of CaO. If the manganese has not been precipitated with the alumina, the very small amount of MnO can be determined colorimetrically in this lime. In general, however, the weight is so small that it may be neglected.

Volumetric Method.—The only advantage presented by the volumetric method[2] is the great saving of time—an important consideration in commercial work. Personally, the author prefers the gravimetric determination as CaO. He is indebted to Miss Keyes for a description of the procedure as used in some commercial laboratories.

Before beginning the operation it is important to fill the Mohr's burette with standard permanganate solution to a definite point, because the titration must be done as soon as the solution boils and must be carried out as quickly as possible.

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[1] Hillebrand (Bull. **700**, p. 141) recommends four hours; six is better. Hillebrand–Lundell (p. 499) do not specify the time.

[2] Mellor, p. 215; Hillebrand, Bull. **700**, p. 147; Hillebrand–Lundell, p. 501; Treadwell–Hall, p. 530; Kolthoff–Furman, Vol. Anal., p. 336.

When the calcium oxalate has been filtered and slightly washed, 100 c.c. of water and 20 c.c. of dilute (1:1) sulphuric acid are added to the beaker in which the oxalate has been precipitated.

The liquid is brought to a boil, by which time the calcium oxalate is entirely dissolved, removed from the flame, and the paper containing the precipitate is dropped into the hot solution. It is allowed to stay for a moment, until most of the precipitate is dissolved, and the paper is then drawn up with a glass rod and made to adhere on the side of the beaker above the liquid.

The solution is titrated immediately, with constant stirring, to the first permanent pink blush. The paper is then pushed down into the liquid to dissolve the small amount of oxalate that it contains, which decolorizes the solution, and the titration is continued very cautiously, drop by drop, to the final end-point. The results are very accurate.

Strontia.[1]—The calcium oxide, as obtained above, contains all the strontia of the rock, but scarcely ever more than traces of the baria. The amount of strontia is always very small, not more than one milligram or less, except in a very few, highly unusual rocks. In most analyses, therefore, it need not be determined, especially as it enters rock minerals as an isomorphous replacer of lime. It will be well, however, to determine it occasionally, as in one or two rocks of a series, since we know little of its relationships to the other constituents. There are no serious errors involved in its determination.

The strontia may be determined by several methods, none of which is entirely satisfactory.[2] The only one that is described here is one that has been in use in the Geological Survey laboratory for many years. It is based on the solubility of calcium nitrate in a mixture of ether and absolute alcohol, and on the insolubility of strontium nitrate in this medium. The method, as here described, differs in small details from that of Hillebrand.

After the lime has been finally weighed, and before it has absorbed any appreciable amount of carbon dioxide from the air, it is slightly more than moistened with a few drops of water in the crucible in which it is weighed. Dilute nitric acid (1:1) is added, drop by drop, until the lime is *just* dissolved. The contents of the crucible are then evaporated to *complete dryness* on the water-bath, and when cold about 10 c.c. of a mixture of absolute alcohol and ether in equal volumes is poured in. The crucible is tightly closed with a well-fitting cork, and laid aside in a cool place for twenty-four hours.

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[1] Classen, 1, p. 797; Fresenius–Cohn, **1**, p. 621; Hillebrand, Bull. **700**, p. 144; Hillebrand–Lundell, p. 490, 744; Mellor, p. 515; Treadwell–Hall, p. 89. L. Duparc, Bull. Soc. Franç. Min., **41**, p. 224, 1919.

[2] The author has found that the method of separation by nitric acid (Cf. Hillebrand–Lundell, p. 491) is entirely unsuited for the small quantities of strontia present in igneous rocks.

The contents of the crucible are then filtered through a 5½-cm. filter and well washed (six times) with the same mixture of absolute alcohol and ether. The filter is allowed to dry in the funnel, after which the strontium nitrate is dissolved in a few cubic centimeters of water which is passed through the filter and received in a 50-c.c. beaker, the filter being washed a few times. A few drops of dilute sulphuric acid are added and then alcohol equal in volume to that of the liquid in the beaker. After standing for twelve hours the precipitated strontium sulphate is filtered off, washed, ignited, and weighed. Its weight is multiplied by 0.56 to obtain that of SrO, which is deducted from that of the lime.

11. MAGNESIA[1]

continu

In rock analysis magnesia has, for many years, always been determined by precipitation as ammonium magnesium phosphate, with subsequent ignition to magnesium pyrophosphate ($Mg_2P_2O_7$). A method that has been recently introduced is its precipitation by 8-hydroxyquinoline, and subsequent weighing as MgO.

The filtrate from the calcium oxalate contains, of the original rock constituents, only the magnesia and alkalies, with some of the manganese and also the nickel and other elements of the sulphide group, if those have not been previously separated (p. 254). There are, of course, also present the alkalies derived from the carbonate fusion and large amounts of ammonium chloride. It is not necessary to remove this last for the determination of magnesia, which is the only constituent that interests us in this filtrate. The operation of evaporating the bulk of the filtrate to dryness, in order to vaporize the ammonium chloride, takes much time.

Errors.—The chief source of error in the determination of magnesia is that already mentioned in connection with alumina, namely, the tendency to precipitation by ammonia along with alumina. This must be prevented by the *presence of sufficient ammonium salts and repeated precipitations*, as has been already described.

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[1] Blasdale, pp. 190–196; Classen, **1**, pp. 830–834; Fresenius–Cohn, **1**, pp. 275–276; Gooch, pp. 81–84; Hillebrand, Bull. **700**, pp. 148–154; Hillebrand–Lundell, pp. 509–514, 745; Mellor, pp. 215–221; Ostwald, pp. 129–151; Stieglitz, p. 165; Treadwell–Hall, pp. 77–80. Of the long list of papers on the determination of magnesium as pyrophosphate there may be cited: Alice W. Epperson, Jour. Am. Chem. Soc., **50**, p. 321, 1928.

An error of less magnitude and importance, but one that must be avoided, is that involved in the precipitation of the ammonium magnesium phosphate, so that the magnesium pyrophosphate is not normal in composition, owing to the presence of magnesium metaphosphate, $Mg(PO_3)_2$, as was pointed out by Neubauer[1] and by Gooch and Austin.[2] This must be corrected by solution of the first precipitate and reprecipitation from the acid solution by a slight excess of ammonia. This error will not affect the other constituents, but will raise the figure for MgO only, and hence the summation will be too high. The error due to this cause will usually be of slight magnitude and seldom of the importance attributed to it by Robinson.[3]

The magnesia will be too low if the precipitate of calcium oxalate has not been dissolved and reprecipitated.

The figure for magnesia will be slightly high if manganese has not been separated previously. If this has not been done, the magnesium pyrophosphate is contaminated with a part of the manganese; and for very accurate work this should be determined colorimetrically in the whole of the magnesium pyrophosphate precipitate dissolved in acid. It may usually be neglected.

There is almost certain to be a loss if the ignited magnesium pyrophosphate is moistened with or dissolved in nitric acid and reignited to render the pyrophosphate white, as is recommended by Fresenius and others, so that this practice should not be followed.[4]

use **Phosphate Method.**[5]—The total filtrate containing all the magnesia may now amount to nearly 1000 c.c.,[6] contained in two

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[1] Neubauer, Z. Angew. Chem., 1896, p. 439.

[2] Gooch and Austin, Am. Jour. Sci., **7,** p. 187, 1899. There is a large literature on this subject.

[3] H. H. Robinson, Am. Jour. Sci., **41,** p. 260, 1916.

[4] Cf. Hillebrand, Bull. **700,** p. 151; Hillebrand–Lundell, p. 511; Mellor, p. 220; Treadwell–Hall, p. 78.

[5] The following is essentially the procedure of the Bureau of Standards. Cf. Alice W. Epperson, Jour. Am. Chem. Soc., **50,** p. 324, 1928.

[6] The volume will be much smaller if the filtrate from the ammonia precipitate has been evaporated to recover alumina (p. 172). In this case two 600-c.c. beakers are to be used.

800-c.c. beakers. To each is added about 50 c.c. of ammonia. A solution of about 3 grams of sodium ammonium phosphate[1] in 50 c.c. of hot water is made up and, after being filtered, is divided between the two beakers. The precipitation should be in a cold solution.

The mixture in each beaker is to be well stirred, and the beakers are laid aside (covered) for at least overnight, and preferably twenty-four hours. here- beakers - 207

At the end of this time the liquid is filtered and the beaker and the precipitate are washed slightly with water containing about five per cent of ammonia.[2] The filtrate is rejected. The precipitate is then dissolved in about 25 c.c. of warm, dilute hydrochloric acid (1:5), the solution being caught in one of the two 800-c.c. beakers. The precipitate adhering to the sides of both is washed down and dissolved in dilute hydrochloric acid, which is passed through the filter, and the beakers and filter are well washed. All this is carried out as described on p. 104.

At the end, the hydrochloric acid solution, which will be in but one of the beakers and should amount to not more than 250 to 300 c.c., will contain all the magnesia. Ammonia is added in *slight excess*, drop by drop with constant stirring. When the precipitate is well formed, a few cubic centimeters of ammonia are added. The liquid is allowed to stand for five or six hours, or overnight. ✓

The final precipitate may be collected in a Gooch crucible or on a paper filter. The latter is to be preferred, on the whole, though it makes little difference which is used. If a Gooch crucible is used, this is prepared and the filtration and ignition are carried out as described on pp. 112–114. If paper is used the precipitate is collected on a 9-cm. filter. As the fine precipitate has a tendency to creep up the glass wall of the funnel, this should be guarded against. The ignition in the moist paper is carried out as with the silica, the paper being *carbonized and burnt away very slowly*, to avoid reduction of the phosphate.[3] ✓

In either case the precipitate is ignited over a Meker burner for ✓

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[1] This was used by Hillebrand. Hillebrand–Lundell (p. 510) recommend diammonium phosphate. The author prefers microcosmic salt, as being more readily obtainable and equally effective if two precipitations are made, as should always be done.

[2] A special 300-c.c. Pyrex glass wash-bottle (p. 44) should be reserved for this use.

[3] The crucible is easily attacked or even ruined by reduction of the phosphate to phosphide, as is apt to happen if the flame is too large. There is no danger of this if the operation is properly carried out. Cf. Hillebrand–Lundell, p. 511.

thirty minutes or more, and reignited to constant weight. Blasting is never necessary; indeed the precipitate should not be blasted because the crucible is apt to be attacked. Prolonged ignition is often needed to obtain a perfectly white product. It should not be moistened with nitric acid to oxidize the carbon, as was said above. The weight of the carbon is so small, in any case, as to be generally negligible, whereas treatment with nitric acid will almost certainly lead to loss.

After cooling in the desiccator, the crucible and its contents are weighed, the gain in weight being $Mg_2P_2O_7$. This is to be multiplied by the factor 0.3621 to reduce it to MgO.

A novice will do well to test the completeness of the separation of magnesia and alumina by examining the solution in which TiO_2 has been determined (p. 190). Alumina and iron are to be precipitated in the whole or an aliquot part of this solution. The precipitate is filtered off, and magnesia, if present, is determined in the filtrate by the method just described, and its weight is to be added to that of the magnesia as determined above, and subtracted from that of the alumina. It is best, however, to do the whole analysis again.

omit

8-Hydroxyquinoline Method.[1]—By the use of this new reagent magnesia may be determined in much less time than by the long-established precipitation as phosphate, and with equal accuracy. Because of the bulkiness of the precipitated magnesium hydroxyquinolate, the method is not suitable for rocks with more than three or at most four per cent of magnesia. It is therefore best suited for such rocks as granite and rhyolite.

The combined filtrates from the calcium oxalate are to be evaporated down to about 300 c.c. and a little ammonia is added. This is then made slightly acid with hydrochloric acid and heated to 60°–70°. An excess, usually 10 c.c., of the solution of 8-hydroxyquinoline (p. 61) is added, the liquid is stirred, and dilute ammonia is slowly added until precipitation is complete and the solution is distinctly alkaline. The liquid will be yellow if there is an excess of the reagent. The bulky precipitate is allowed to settle, the clear supernatant liquid is tested with a few drops of the reagent, and the whole is filtered and well washed with hot dilute ammonia (1:40). The filtration may be carried out in paper,[2] but as the precipitate is bulky and hard to wash and to dry, it is best to use a Gooch crucible of platinum or vitreosil with asbestos.[1]

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[1] Hillebrand–Lundell, p. 116. J. Robitschek, J. Am. Ceram. Soc., **11**, p. 590, 1928.

[2] This cannot be used unless the precipitate is to be ignited to MgO.

The precipitate may be weighed as quinolate, $Mg(C_9H_6ON)_2$, by drying it at 110°–140° C. and weighing. The factor for MgO of the quinolate is 0.1291. It may also be ignited to constant weight and weighed as MgO. We have found that the addition of oxalic acid before ignition, which is recommended by some, is *not necessary*, as did others in the determination of beryllium.[2]

There are no special precautions to be taken in the ignition, as is the case with the cupferron precipitate of titanium, except that the heating should be slow at first. The author prefers this ignition of the precipitate to MgO to the above described method of weighing the precipitate as quinolate.

The MgO may also be determined volumetrically in the quinolate,[3] by the use of potassium bromate. This is more rapid, and is advantageous in industrial work. But for scientific work the gravimetric method is better, as there is no need to make up the standard bromate-bromide and thiosulphate solutions.

continue

12. Ferrous Oxide[4]

FeO

Ferrous oxide is determined in a separate portion of rock powder. For rocks such as granites or rhyolites, that contain but little iron, it is well to use one gram; but for most rocks one-half gram will be an appropriate amount.

Inasmuch as the titration with permanganate is best done with ferrous sulphate, and as no igneous rock is composed of minerals that are entirely soluble in sulphuric acid, it is necessary to add hydrofluoric acid to this to decompose the rock for the determination of ferrous oxide.[5]

The operation must also be carried out in a non-oxidizing atmosphere. The methods to attain these objects are of two kinds: the operation may be carried out under atmospheric pressure, or in a sealed tube under high pressure. We shall deal first with the former type.

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[1] A Jena glass filter-crucible may be used, or a Jena glass Gooch (with asbestos) if the precipitate is to be weighed as quinolate. These cannot be used if it is to be ignited to MgO.

[2] Cf. Kolthoff and Sandell, Jour. Am. Chem. Soc., **50**, p. 1902, 1928.

[3] Cf. Hillebrand–Lundell, p. 116.

[4] Classen, **2**, pp. 620–623; Hillebrand, Bull. **700**, pp. 189–207; Hillebrand–Lundell, pp. 769–785; Mellor, pp. 461–466; Treadwell–Hall, pp. 432–433. L. Duparc, Bull. Soc. Franç. Min., **41**, p. 237, 1919.

[5] This is necessary even with minerals—such as olivine, anorthite, or leucite—which are wholly soluble in hot sulphuric acid, because of the possibility of the presence of insoluble inclusions.

The method described in most textbooks, and indeed the only one in some of them, is a modification of a method proposed by Cooke as far back as 1867.[1] A modification of this method was used in the U. S. Geological Survey laboratory for many years, but it has now been abandoned in favor of the modified Pratt method.

In recent years electrometric methods have been much used, one especially for the determination of the iron oxides. As the author had had no experience with these they will not be described here.[2]

Errors.—The correct determination of ferrous oxide has long been one of the most difficult and uncertain points in the analysis of rocks. The chief difficulty lies, of course, in the solution of the material without oxidation of the ferrous oxide to ferric.

It was formerly thought to be imperative that, whatever the method employed for the determination of ferrous oxide, the rock powder should be extremely fine, and the use of specially ground powder was previously advocated by Hillebrand and also by the author in the first edition of this book.

Mauzelius[3] has, however, shown that there is a decided tendency to oxidation of the ferrous iron during grinding, and that this becomes the more marked the longer the grinding and the finer the powder, so that he recommends the use of as coarse a powder as will be completely attacked by the acid. These conclusions have been confirmed by Hillebrand,[4] who attributes the oxidation to strong local heating at the moment of fracture of the grains under the pestle. The oxidation can be diminished or even completely avoided by grinding under inert liquids, as water, carbon tetrachloride, or alcohol, the last being the most suitable. It must be observed, as regards Hillebrand's investigations, that the times of grinding used by him were very long, at least two hours or more in some cases, a mechanical grinder being used and the powder being reduced to an extreme degree of fineness. When the grinding was half an hour or less the oxidation seems in general to have been negligible.

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[1] J. P. Cooke, Am. Jour. Sci., (2), **44**, p. 347, 1867.

[2] Hostetter and Roberts, Jour. Am. Chem. Soc., **41**, pp. 1337–1357, 1919; H. S. Roberts, *ibidem*, p. 1358; Kolthoff and Furman, Potentiometric Titrations, New York, 1926; Farnsworth, pp. 119–148.

[3] R. Mauzelius, Sver. Geol. Unders., Aarbog, I, No. **3**, 1907.

[4] Hillebrand, Jour. Am. Chem. Soc., **30**, p. 1120, 1908, and Bull. **700**, pp. 60, 189–192; Hillebrand–Lundell, pp. 769–771; Mellor, p. 124; Treadwell–Hall, p. 52; Sosman and Hostetter, Trans. Am. Inst. Min. Eng., p. 919, 1917.

It follows from these investigations that to obtain correct results for FeO, the rock powder must be as coarse as is consistent with complete solution in the acids employed, and that long-continued grinding is to be avoided in preparing the sample. In the method for preparing the sample described above (p. 83) the time spent in crushing is very short and the grinding of the final small residue lasts only five minutes or less, so that the oxidation of the resulting powder is negligible. The author has also found that such a powder is easily and completely attacked and dissolved by the Pratt method in the case of all rocks tested, ranging from rhyolites and granites to basalts and peridotites. The main portion of the sample will therefore serve for the ferrous oxide determination *without further grinding.*

Such fine grinding may seem to be called for especially with rocks that contain considerable ferro-magnesian minerals, such as pyroxenes, biotite,[1] and amphibole, which are attacked with difficulty by the acids used. As an illustration of the data obtained in practice which have led the author to the conclusion that special grinding for FeO is unnecessary, we cite two determinations of FeO made on the same sample of aegirite from Laven.[2] The first was made without, and the second with, fine grinding. The results were, respectively 6.85 and 6.88 per cent FeO.

For ordinary rock analysis the grinding of the powder under alcohol to prevent oxidation is not to be recommended, as it involves some sources of error and loss of time through drying, and it is not necessary.

There is always the possibility of partial oxidation, both by atmospheric oxygen and by the sulphuric acid, during the decomposition, and this may be very serious. It can be guarded against and eliminated by careful manipulation, but uniform success as regards this point is to be attained only by care, practice, and experience.

If sulphides, vanadium as V_2O_3, or organic matter are present they will reduce the permanganate and render the results too high. Organic matter is not to be generally expected in igneous rocks, and in the great majority of them sulphides and vanadium are only present (if at all) in amounts so small as to make their influence quite negligible. The point is discussed by Hillebrand,[1] who may be consulted for details. Hillebrand, it seems to the author, attributed too much importance in general to the influence of sulphides and of vanadium on the determination of ferrous oxide in igneous rocks. The effect of sulphides is apt to be most marked with metamorphic rocks, or specimens collected in mining regions. If any considerable amount of sulphides is present there would seem to be no method now known to obtain correct figures for ferrous oxide. The percentage of vanadium is almost always so small in igneous rocks that its influence may safely be left out of account.

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[1] Although the amount of biotite in the rock powder may appear to be great, yet the flakes are so thin that they are readily attacked.

[2] Washington and Merwin, Am. Mineral, **12**, p. 249, 1928.

The presence of hydrofluoric acid in the solution used for the determination of FeO is a very important factor.[2] This not only renders the ferrous sulphate unstable, but causes the end-point to be transitory and uncertain.

Bivalent manganese is readily oxidized by permanganate, especially if hydrofluoric acid is present, so that if the rock contains much iron the considerable amount of manganous sulphate formed renders the end-point fleeting and the titration somewhat uncertain.[3]

Thus, the presence of both hydrofluoric acid and manganous sulphate is deleterious, and as they are both necessarily present in the analysis of rocks, it is obvious that the determination of ferrous oxide in them must sometimes be looked on with some suspicion as to its accuracy.

Several suggestions have been made to counteract these deleterious effects, that of hydrofluoric acid especially. The matter has been thoroughly investigated by Barneby[4] who studied the effect of a number of additions to counteract the detrimental effect of hydrofluoric acid. He finds that most of those proposed are not entirely effective or satisfactory, but that the presence of boric acid in excess, by forming fluoborates, renders the solution stable in the presence of air, and gives a definite and lasting end-point.[5] Indeed, the addition of boric acid seems to have solved the problem of the exact titration of ferrous oxide in silicate rocks.

It must not be thought, however, that it is essential, because exact and concordant determinations can be made by an experienced analyst without its use. Thus, Hillebrand[1] says: "It is possible to titrate ferrous iron in presence of sulphuric and as much as 5 to 7 c.c. of 40 per cent hydrofluoric acid in a total volume of 200 to 400 c.c. almost if not quite as exactly as in sulphuric acid alone, provided that the iron solution is diluted with air-free water and the titration is made immediately after adding the hydrofluoric acid and with all possible dispatch." For the beginner, however, and even for the experienced analyst, it will be well to follow Barneby's recommendation and titrate in the presence of boric acid.

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[1] Hillebrand, Bull. **700**, pp. 201–213; Hillebrand–Lundell, pp. 778–780.

[2] Hillebrand, Bull. **700**, pp. 197–199; Hillebrand–Lundell, pp. 775–776; Mellor, p. 465.

[3] Cf. Hillebrand, Bull. **700**, p. 197; Hillebrand–Lundell, p. 775.

[4] O. L. Barneby, Jour. Am. Chem. Soc., **37**, p. 1481, 1915.

[5] It also prevents the glass from being attacked by the hydrofluoric acid.

There is a slight tendency to minus errors in the determination of ferrous oxide, but if properly carried out the method as here described yields very accurate results.

Simple Method.—There are several modifications of the method of decomposition by a mixture of hydrofluoric and sulphuric acids, which differ in comparative simplicity, and to some extent in accuracy. The simplest, and the one which the author has found to be sufficiently accurate for most purposes, and by far the most rapid, will be described first. This is essentially the method first tested by Pratt, and is simpler than the one now adopted by the U. S. Geological Survey. The author has found it to give accurate and concordant results.

About half a gram of the rock powder[2] is weighed into a 30- or 35-c.c. platinum or palau crucible,[3] the cover of which must fit closely. It is moistened with a little water, this being blown gently against the side of the crucible, the wash-bottle tip, after being filled with water, inserted beneath the slightly raised cover. In this way the mass may be moistened without blowing out any of the rock powder. When the powder is thoroughly wet and pasty, a few small coils of platinum wire or scraps of platinum foil are dropped in, to prevent bumping. If carbonates are present in the rock, a few drops of very dilute sulphuric acid are poured in and the cover is quickly put on, until effervescence ceases.

Before this the nearly full hot-water wash-bottle is heated until the water boils vigorously so as to drive out all dissolved air; after which it is cooled under the tap.

In another platinum crucible or the small basin, about 10 c.c. of warm dilute sulphuric acid is made by pouring 5 c.c. of the concentrated acid into 5 c.c. or so of cold, boiled water. Into this is poured about 5 c.c. of hydrofluoric acid, an operation that must be done with caution and in small portions at a time. Hydrofluoric acid causes painful and lasting burns and *too great caution cannot be exercised in handling it.*

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[1] Hillebrand, Bull. **700**, p. 197; Hillebrand–Lundell, p. 775.

[2] The rock powder that serves for the main portion is to be used; it should not be specially ground.

[3] A large crucible is necessary to prevent boiling over.

The crucible containing the wet powder is placed in a triangle resting on a ring-support.[1] It must not be pressed into place, but is laid in loosely so that the crucible may be easily taken out. The ring should be at a height so as to bring it about 10 cm. above a small Bunsen burner flame. The Bunsen burner is lighted, its flame adjusted to a height of about 4 cm. and it is placed near by, not beneath the crucible.

The crucible is now uncovered with the tongs in the left hand, enough of the warm mixture of sulphuric and hydrofluoric acids is quickly but gently poured in to fill the crucible about one-third full, and the cover is quickly put in place, but not pressed down tight.

With the Bunsen burner flame waved below the crucible, the liquid is heated until it just begins to simmer, but not to boil, then the burner is put in place beneath the crucible. The points to be attended to are that the hot liquid should begin to steam and so replace the air in the crucible as soon as possible, and the liquid should be kept *simmering continuously,* but without any bumping or foaming which might lead to loss by spattering or boiling over.

This may be attained by properly adjusting the size of the flame and the height of the crucible above it. These will vary, of course, with different conditions, but the author has found that with a flame about 4 cm. high the 35-c.c. crucible used for this operation should be about 15 cm. above its tip. Some practice is needed, but the right conditions will soon be learned. At first the crucible must be constantly watched, and the operation proceeds properly when the liquid is heard to be simmering gently and a little white vapor issues from around the cover. *The liquid must never "bump."*

When all is proceeding well, or before the acid is added, a 600-c.c. beaker is slightly more than half filled with cold boiled water, about 10 c.c. of dilute (1:1) sulphuric acid is poured in, and (following

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[1] The operation may be carried out on the workbench (the author's usual practice), but may also be conducted in the hood. There should be no drafts during the heating of the liquid.

Barneby) 10 c.c. of saturated boric acid solution is added.[1] The beaker is placed on the bench to the right of the burner.

The simmering is continued for six to eight minutes, according as the rock is largely feldspathic or is high in ferromagnesian minerals. For the great majority of rocks the author finds that six minutes is ample for complete decomposition, and yet not long enough to cause sensible oxidation of the ferrous oxide by the hot sulphuric acid. If the rock is basic, however, especially when it contains much augite or ilmenitic iron ore, such as do some basalts, it is best to boil the powder for ten minutes.[2]

When the allotted time is up the crucible is firmly grasped in a pair of Blair's tongs, rather above the center, and is plunged quickly but without any splashing into the water in the open 600-c.c. beaker standing at hand, and the tongs are immediately withdrawn. The tongs are best provided with platinum shoes[3] (p. 38), but shoes of chromel or even German silver or brass of the same shape would answer.[4]

Tongs of the ordinary form are not well adapted to this determination, as it is difficult to grasp the covered crucible with the ends without slipping or letting the crucible tilt. Such tongs may, however, be used by grasping the crucible between the *bowed* portions. In this case, it is well to have the points upward and to use a sufficiently large beaker, with enough water to cover the crucible, and held somewhat tilted.[5] The tongs for this must be of German silver or brass, and are to be rinsed off into the beaker immediately after withdrawal. This way of using the ordinary tongs has been found to be much more practical and safe than the use of two handle portions of wooden test-tube holders, recommended in previous editions, and better than Mellor's suggestion of a loop of platinum wire, which is apt to slip.

The contents of the beaker are titrated with standard permanganate solution *immediately* after the crucible has been placed in it; the burette having been already filled, weighed, and put in position. During the titration the liquid is gently stirred with a glass rod, and the crucible and its cover are moved about, so that the permanganate may reach all parts of it and the contents of the crucible are thoroughly mixed with the liquid in the beaker.

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[1] This is preferable to solid boric acid.

[2] Hillebrand (Bull. **700**, p. 200) and Hillebrand–Lundell (p. 778), obtained excellent results with ten minutes' heating, using a 100-c.c. crucible.

[3] Such tongs are figured by Hillebrand, Bull. **700**, p. 32; Hillebrand–Lundell, p. 21.

[4] It would be well for the dealers to sell tongs of such non-ferrous alloys for this determination, as well as for other purposes. For the ferrous iron determination they must not be of steel or iron.

[5] It is well to practice this operation on a crucible half full of water.

The titration is carried out to the first pink blush through the whole liquid that persists for some seconds in spite of stirring. With boric acid present the end-point is sharp; in its absence the end-point is more difficult to arrive at. After titration the contents of the beaker should be examined to ascertain if decomposition has been complete, which is shown by the absence of hard, gritty, or dark particles. If such are present the operation must be repeated, using another weighed portion of rock powder, the heating being continued for a longer time, or the portion of powder being more finely ground.

With rocks that contain much lime or magnesia the liquid may be somewhat turbid. This does not indicate that the rock is not wholly decomposed, but is due to the formation of calcium sulphate or the fluorides of calcium and magnesium.

The burette is now weighed, or the reading of the Mohr's burette taken. The loss in weight (or the number of cubic centimeters used) is multiplied by the FeO value of 1 gram (or c.c.) of the standard permanganate solution to arrive at the weight of the FeO. The loss in weight (or the number of cubic centimeters used) is also to be multiplied by the value for Fe_2O_3 that corresponds to that of the FeO. The weight of the rock powder taken for the main portion, in which the total iron oxides have been determined as Fe_2O_3, is multiplied by this, and the product is subtracted from the weight of the total iron oxides (p. 188). The remainder is the weight of the Fe_2O_3 of the rock.

It may sometimes happen, especially with rocks that contain much nephelite or minerals that gelatinize with acids, that the powder cakes at the bottom of the crucible, preventing complete decomposition. This is usually due to the fact that the powder has not been thoroughly stirred up with enough water before the addition of the mixed acids. In such a case the whole operation must be repeated until successful, or the rock powder may be mixed with powdered quartz,[1] as was suggested by Dittrich.[2]

Pratt's Method.—The simple method described above was modified by Pratt,[1] by allowing a current of carbon dioxide to flow into the crucible during the boiling by a platinum tube passing through a hole in the cover. As modified by Hillebrand,[2] the rock powder in the crucible is mixed with 10 c.c. of dilute sulphuric acid, the crucible is placed in a triangle over the burner, and the air is replaced by carbon dioxide, which enters beneath the lid slightly raised on one side. Before the liquid boils the gas current is stopped and the well-fitting cover is lowered; then 5 to 7 c.c. of strong hydrofluoric acid is quickly poured in through an opening formed by drawing the lid a trifle to one side, the lid is replaced, and the boiling is continued for the requisite time. The rest of the operation is as above. This method has certain advantages over the first, but there seems to be little to choose between them, as far as accuracy is concerned.

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[1] A clear quartz crystal should be used; not sand, which contains some iron.

[2] M. Dittrich, Berichte, **44**, p. 990, 1911. Cf. Mellor, p. 462, note 7.

Soule[3] suggests that the solution in mixed sulphuric and hydrofluoric acids be carried out in a 250-c.c. Erlenmeyer flask of Pyrex glass or fused silica in the presence of a stream of CO_2. This obviates the need of a capacious platinum crucible, but a correction must be applied when Pyrex is used. In view of the simplicity and accuracy of the first method described above, such a modification seems to be uncalled for.

Mellor (p. 464) heats the crucible beneath a 15-inch funnel (paraffin-coated), through which a stream of carbon dioxide flows. The crucible is supported in a hole in a square of asbestos board, on which the inverted funnel rests. This is simple, and should be effective,—but it is quite unnecessary.

If an appreciable amount of sulphur as sulphides exists in the rock, regard must be had for the iron in combination with it. If pyrrhotite is the only sulphide present, this will be decomposed by the mixture of acids in the determination of ferrous oxide, and the iron will appear as FeO. The sulphur should be stated as S in the analysis, not as FeS_2 or Fe_7S_8 (p. 25). If the only sulphide is pyrite, this will not be attacked in the determination of FeO, but the iron in this mineral will appear as Fe_2O_3. This may be accorded treatment similar to the iron in pyrrhotite, (p. 145). If both sulphides are present, it will be impossible to estimate the real correction unless the relative amounts of the two minerals are known.

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[1] J. H. Pratt, Am. Jour. Sci., (3) **48**, p. 149, 1894.

[2] Hillebrand, Bull. **700**, p. 200; Hillebrand–Lundell, p. 781.

[3] B. A. Soule, Jour. Am. Chem. Soc., **50**, p. 1691, 1928. Hillebrand–Lundell, p. 785.

Fortunately this is seldom needed, and in general the amount of sulphides is so small that corrections for it are not often necessary.

Cooke's Method.[1]—Some modifications of Cooke's method are briefly described here, as it figures prominently in the textbooks. It was long ago abandoned by the author, after many trials, and has likewise been replaced by the modified Pratt method in the laboratory of the U. S. Geological Survey, after thorough investigation by Hillebrand.[2] The Cooke method, whether in the original form or as modified by Treadwell and others, demands special and elaborate apparatus; takes an inordinate amount of time; the decomposition is very apt to be incomplete; and, most serious objection of all, some oxidation is almost certain to occur during the prolonged heating.[3]

The modification of the Cooke method formerly used by the Geological Survey, as described by Hillebrand, is as follows. A small water-bath is used,[4] with a single opening and a trough-like depression around the specially made cover. Into this trough water constantly drips, thus making a secure water joint and keeping the bath full. CO_2 is kept flowing into the air above the water in the bath, replacing it.

The large platinum crucible containing the weighed rock powder mixed with dilute sulphuric acid is placed in the opening, and is covered by a glass funnel, the stem of which has been cut off near the flare. The burner beneath it is then lit. When the air in the funnel and in the crucible has been replaced by CO_2, 5 to 7 c.c. of strong hydrofluoric acid is poured into the crucible through a special funnel of platinum or rubber inserted through the cut-off stem.

When steam issues strongly from the funnel the CO_2 current is cut off, and the apparatus is left to itself for an hour, except for an occasional stirring with a long platinum rod inserted through the opening of the cut-off funnel stem. When decomposition is complete, the CO_2 current is turned on again, the burner is extinguished, and the water flow in the bath is increased to the capacity of the outlet. In fifteen minutes the crucible and contents should be cool, when the rod is removed and placed in the titration beaker containing some cold boiled water. The crucible and contents are transferred to this and the titration is carried out as above.

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[1] J. P. Cooke, Am. Jour. Sci. (2) **44,** p. 347, 1867; Hillebrand, Bull. **700,** p. 204; Hillebrand–Lundell, p. 782; Mellor, p. 462; Treadwell–Hall, p. 432.

[2] Hillebrand, Bull. **700,** pp. 190, 200; Hillebrand–Lundell, p. 777.

[3] Hillebrand, Bull. **700,** pp. 190, 197; Hillebrand–Lundell, pp. 775, 777.

[4] The diameter of the bath is only about three times that of the crucible.

For a description of Treadwell's method for FeO the student may best consult his textbook.[1] A large lead vessel and a paraffin bath are needed.

After reading the description of either modification of the Cooke method, noting the complexity of the apparatus needed (especially that of Treadwell), the length of time and the danger of oxidation involved, one should need no argument to be convinced of the serious defects of the Cooke method and of the great superiority of the Pratt method in either of its modifications.

The Mitscherlich method[2] consists in decomposing the rock powder by dilute sulphuric acid in a sealed glass tube. It is open to many objections: liability of the glass to be attacked; difficulty of ascertaining when decomposition is complete; the great trouble and time involved in the procedure; with other minor ones. For the analysis of rocks it should never be used and need not be considered here.

13. ALKALIES[3]

Several methods are available for bringing the alkalies of silicates and silicate rocks into solution free from other constituents for the separate determination of the K_2O and Na_2O. For this last there are now two prominent methods, the chloroplatinate and the perchlorate.

In the older (Berzelius) method the rock powder is decomposed by a mixture of sulphuric and hydrofluoric acids, or by fusion with bismuth, lead, or boric oxides, digestion with the acid mixture being that which was mostly used. The solution so obtained is treated successively with ammonia and with ammonium oxalate to remove silica, alumina, iron, titanium, phosphorus, and lime. The magnesia is separated by one of several reagents[4] (most often mercuric oxide), the sulphuric acid is removed by lead acetate or by barium chloride, and the alkalies are determined in the filtrate as in the method described below.

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[1] Treadwell–Hall, p. 434; Mellor, p. 462.

[2] For a discussion of this method see Hillebrand, Bull. **700**, pp. 193–106; Hillebrand–Lundell, pp. 771, 773.

[3] For the determination of the alkalies in silicate rocks see: Classen, **2**, pp. 613-615; Fresenius–Cohn, **1**, pp. 519–520; Hillebrand, Bull. **700**, pp. 207–213; Hillebrand–Lundell, pp. 783–795; Mellor, pp. 222–227; Treadwell–Hall, pp. 425–427. L. Duparc, Bull. Soc. Franç. Min., **41**. p. 227, 1919.

[4] Duparc (Bull. Soc. Franç. Min., **42**, p. 235, 1919) suggests the use of ammonium arsenate.

These procedures are complex and take much time. Furthermore, the final solution is certain to be contaminated by unknown amounts of alkalics taken up from the glass vessels and derived from the reagents used. There may also be loss of alkalies during the blasting that is called for with certain of the fluxes used. Such methods should never be used for the analysis of rocks or of silicate minerals,[1] and the simple, rapid, and accurate Lawrence Smith method for decomposing the rock should be unhesitatingly adopted.[2] This is all the more called for because, with proper management, an ordinary platinum crucible can be used instead of the special form devised by Smith.

Lawrence Smith Method.—The best method is that of J. Lawrence Smith.[3] The rock is decomposed by heating with calcium carbonate and ammonium chloride; the cake is leached with water from the insoluble silicate and aluminate of calcium, and carbonates of iron, calcium, and magnesium; and the alkalies are brought into solution as chlorides, the lime in solution is precipitated by ammonium carbonate; the ammonium salts are expelled by heating the evaporated filtrate; and the final separation of the alkalies is effected by chloroplatinic acid or by perchloric acid.

The advantages of this method are: its simplicity and the short time needed, the manipulations being few, and a day and a half or two days being ample for the complete determination;[4] the separation of magnesia at the start, which is a troublesome constituent to separate from the alkalies by the other methods; the small chance of introduction of alkalies from reagents or glass vessels; and, finally, its great accuracy, which is superior to that of the older methods.[5]

The chief objection that can be urged against this method, as compared with the others, is the difficulty of obtaining a calcium carbonate entirely or negligibly free from alkalies. The amount of these, however, is easily rendered negligibly small by sufficient washing, and it is a constant error, the correction for which can be safely applied when once determined for the stock of calcium carbonate. Even if this is not done, however, it is certain that the errors involved will be less, if care is taken in the preparation of the calcium carbonate, than those incident to any of the older methods. As was pointed out by Smith, his method converts "the most difficult part of the analysis of a silicate into the easiest."

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[1] Except possibly in rare and exceptional cases.

[2] J. Robitschek (J. Am. Ceram. Soc., **11**. p. 391, 1928) suggests the use of 8-hydroxyquinoline for the determination of the alkalies. For accurate work this is not to be recommended, because of the contamination from the glass vessels and reagents, if for no other reason.

[3] J. L. Smith, Am. Jour. Sci., **1**, p. 269, 1871.

[4] Not more than four hours are required for the active operations.

[5] Cf. J. L. Smith, *op. cit.*; Hillebrand, Bull. **700**, p. 207; Hillebrand–Lundell, p. 787; M. Dittrich, Neues Jahrb., 1903, **2**, p. 81. L. Duparc, Bull. Soc. Franç. Min., **42**, p. 169, 1919.

The Lawrence Smith method is the only one that has been used by the chemists of the U. S. Geological Survey and by the author and in the Geophysical Laboratory. It is the method that is always employed in this country. In Europe, on the other hand, it seems to be less well known, or at least less often used, but its undoubted merit and superiority over the older Berzelius method is now generally recognized. The chief reason why it is sometimes not used is the belief that a special form of platinum crucible, such as was suggested by Smith, is necessary to obtain accurate results. This form of crucible is, however, *not necessary,* and equally accurate results are obtained with a platinum crucible of the usual form, provided proper care is exercised during the ignition.

Errors.—An inherent error is that it is difficult to obtain the calcium carbonate entirely free from alkalies, very small amounts of sodium and much less of potassium being present. These can be reduced to negligible amount by thorough washing of the properly precipitated carbonate with hot water. If the amount of alkalies present is very small the error is of slight importance, as their weight calculated as chlorides can be determined once for all in the stock of calcium carbonate and an appropriate correction is safely applied. (See p. 59.) If the calcium carbonate is properly prepared and well washed, the error involved by neglect to apply this correction will be negligible.

Another source of error is the retention of alkalies in the fused cake. This has been investigated by Holland[1] and by Connor.[2] Their results show that there is possibility of such a loss, as was already pointed out by Smith. As their results differ in magnitude, they indicate that the magnitude of the loss depends on the manipulation. As Hillebrand suggests,[3] the somewhat high retained soda and potash observed by these workers is probably due to an insufficient temperature. Hillebrand-Lundell state that the residue seldom needs retreatment, and they give the results of tests on this matter.

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[1] See Mellor, p. 225.

[2] M. F. Connor, XII Cong. Geol. Int., C. R., p. 888, 1914.

[3] Hillebrand, Bull. **700**, p. 209; Hillebrand–Lundell, p. 790.

The author's experience is similar to theirs. If the procedure is properly carried out the loss should be negligible, but in highly accurate work the washed cake should be again heated with some ammonium chloride after thorough regrinding.

Overheating of the crucible during the sintering with calcium carbonate; overheating or too rapid heating of the basin during the driving off of the ammonium chloride, or of the crucible in drying the mixed chlorides; are all liable to lead to vaporization of the sodium and potassium chlorides and to low resuts. These can be entirely prevented by careful attention to the conditions of heating as described on later pages. Again, low results will be obtained if the original mixture is underheated, because the rock powder is not entirely decomposed. This should be ascertained by seeing if the residue from the first filtration is entirely soluble in warm dilute hydrochloric acid, leaving no unattacked mineral, except (rarely) a few small black grains of ore that dissolve but slowly. Loss by decrepitation of the chlorides is to be guarded against.

Shannon[1] has recently called attention to a source of error that has been generally disregarded. This is the contamination of the liquid by the ammonium chloride in the laboratory atmosphere after the addition of the chloroplatinate reagent. This will form ammonium chloroplatinate which, being insoluble in alcohol, will be weighed with the potassium salt, thus giving a higher value for the percentage of potash and a correspondingly low value for that of soda. If the liquid is allowed to stand for a considerable time in such an atmosphere before filtration of the chloroplatinate the error may be serious.

Another error is that introduced by not thoroughly mixing the rock powder with ammonium chloride and calcium carbonate. Decomposition will thus be incomplete, leading to low values for both the alkalies.

The weight of the carbon sometimes found in the final mixed chlorides is so small as to be negligible, as was shown by Smith and confirmed by the author's own experience.

Procedure.—For the determination of the alkalies a *specially ground* portion of rock powder is to be used. Although Smith states that this is not necessary in all cases, yet it is certainly advisable, because complete decomposition can thus be secured at a lower temperature and with more certainty than if the powder is coarse.

A little more than one gram of the rock powder is ground down by hand in the small (9-cm.) agate mortar, the grinding being continued until a small pinch causes no gritty feeling when rubbed on a tender part of the skin, such as the web connecting the thumb and the index finger, or the inside of the wrist. It is then placed in a small special specimen tube.[1] No appreciable error due to partial oxidation of the FeO is to be feared by this grinding, and it does not involve great chance of loss of the fine powder incident to the method of first weighing out the coarse powder and subsequent grinding as advocated by Hillebrand. About one-half of this powder will serve for the ferrous oxide determination, if such specially ground powder is to be used for this. About one-half gram is used for the alkali determination.

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[1] E. V. Shannon, Am. Min., **12**, p. 411, 1927; Hillebrand–Lundell, p. 519.

As the rock powder has to be more than ordinarily well mixed with the flux, the preparation of the portion demands a procedure different from that used for mixing the portions for other constituents.

The portion for the determination of the alkalies is to be weighed by the method of subtraction, not by the direct method used for the main portion.

The small tube containing the specially ground powder is wiped perfectly dry, placed on the balance-pan on the small frame intended for this purpose and is weighed.

After weighing, and noting the weight as Tube + subst., a half-gram weight is removed from the right-hand pan, and about one-half gram of powder is carefully poured out into the platinum basin.[2] This must be done with care to avoid any loss of powder, and when a sufficient quantity has been poured out, the tube is to be gently tilted up and lightly tapped to bring the powder down toward the bottom, the mouth being held over the basin. Not more than 0.6 gram need be taken, but not less than 0.45 gram. One-half gram is quite sufficient to yield results fully as accurate as one gram, and the consequent saving of platinum, as well as the shortening of the time needed for the determination, are rather important considerations. The tube (still uncorked) is then weighed again, and the difference between this weight, recorded as Tube — subst. and the former, gives the weight of powder taken.

Just as with the weighing out of the powder for the sodium carbonate fusion it may be necessary to take out and weigh additional small portions several times. One should endeavor to get the final weight only slightly more than, or nearly one-half gram without undue loss of time. A little practice enables one to do this quickly.

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[1] This tube is conveniently kept in the balance-case, and its approximate weight should be known.

[2] Before pouring in the rock powder it is best to warm the platinum basin to drive off any adherent moisture, and allow it to cool.

If much too much powder has been poured out the weight must not be lessened by removing any of the powder with the spatula and placing it in the tube, because this can not be done without loss. In such a case, it is best to make the determination on the somewhat too large amount, which will not be objectionable, or the powder is poured back into the tube, the basin is carefully wiped out, and the weighing is done again, more care being taken this time in pouring out the powder.

One must be especially careful to avoid any loss by wafting away of the fine powder. The breath should not be directed toward the basin while the powder is being poured out, and the basin is to be covered with a watchglass immediately after.

The balance-pans are then cleared of tube-stand and weights, the pair of balanced watchglasses are put on the pans, and an amount of *dry* ammonium chloride equal to that of the rock powder taken is weighed out. It is not necessary that this weight should be exact, and it may be a decigram or so more, but it should not be less. The chloride is poured into the basin, above the heap of rock powder, but very slowly, to avoid loss. This may be done by sliding back the coverglass leaving a sufficiently large opening through which the reagent may be poured.

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The use of the platinum basin is preferred as a mixing vessel[1] to that of a large agate mortar, as recommended by Hillebrand, because, although the mixture may be made as thorough, there is less liability to loss owing to the high sides of the basin, and because the mixed powders are transferred far more easily and safely from the basin than from the mortar. The powder should be ground specially fine *before weighing,* instead of after, as recommended by Hillebrand, because the latter order is almost certain to lead to loss.

The rock powder and the ammonium chloride are thoroughly mixed in the basin by rubbing with the small agate pestle. This mixing must be very thorough and must be effected without any loss of powder. Attention should be paid to the powder at the sides as well as at the bottom of the basin.

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[1] The use of a porcelain basin as suggested by Smith is not advisable, because of the danger of contamination from the glaze. A fused silica basin of the right size serves very well.

An amount of calcium carbonate equal to eight times the weight of rock powder (about four grams) is then weighed on one of the watchglasses. If a correction for the small amount of alkalies present is to be made, this weighing should be carried out to centigrams; if not, the weighing need only be approximate, but the weight should be more, rather than less, than the required amount. With basic rocks five or six grams should be used, to prevent fluidity during the heating. A small amount of calcium carbonate is transferred with the platinum spatula to an unweighed 30-c.c. platinum (or palau) crucible, just enough to cover the bottom, and pressed lightly down with the small agate pestle. This prevents adhesion of the cake to the bottom of the crucible.

After the rock powder has been mixed with the ammonium chloride, this mixture is mixed with the greater part of the calcium carbonate, also in the platinum basin. It is best to add the carbonate in two or three small portions; and the rubbing with the pestle after each addition must be carefully and thoroughly done. The object is to have, so far as possible, some ammonium chloride and calcium carbonate in contact with each particle of rock. An epicycloidal movement is effective. *This thorough mixing in the basin is of the utmost importance;* because otherwise decomposition will probably not be complete.

When the mixing is considered complete, it is well to continue it for a few minutes longer. The pestle is laid down with its lower end in the watchglass, and the mixture is poured cautiously through the lip of the basin into the crucible.[1] This transfer is aided by the platinum spatula in brushing down small lumps and patches, and by final tapping of the spatula on the inside of the basin, so as to cause the whole to pass through the lip without loss outside the crucible. The powder in the crucible is then smoothed down with the spatula, the remaining carbonate is poured into the basin, and the latter rinsed with it by means of the pestle, which is also cleaned at the same time. The spatula is cleaned by rubbing it against the carbonate in the basin, and the final portion of this is transferred as before into the crucible.

If the rock is specially ground as fine as has been described, the decomposition will be complete at a temperature not high enough to vaporize the alkali chlorides. *An ordinary crucible with a well-*

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[1] The crucible should be placed on a 6-inch square of clean paper, so that any powder falling outside it may be recovered. This should never happen.

fitting cover may therefore be employed, instead of the capped, long conical one recommended by Smith and by Hillebrand, which permits a higher temperature for the sintering. It is well to know that *perfectly satisfactory results may be obtained with an ordinary crucible.*

In order to minimize or prevent loss by volatilization of the alkali chlorides it is best to insert the ordinary crucible in a circular hole made in a thin square plate of fused silica or of asbestos board, the diameter of the hole being such as to fit the crucible about one-third from the bottom. Also, a small platinum basin or 30-c.c. Pyrex beaker may be placed on the crucible cover, which will condense on the bottom of the cover any volatilized chlorides. The water will not boil if the perforated plate is used.

If the long, narrow Smith form of crucible is used, the process of transfer is somewhat different. A little calcium carbonate is placed in it, to cover the bottom and prevent adhesion of the cake. The mixed powder in the basin is poured onto a small square of smooth glazed paper, and from this into the narrow crucible, as pouring it directly from the basin is difficult and there is liability to loss. The crucible is then inserted in the round hole bored (at a slight downward angle) in a small fire-clay cylinder, as figured by Hillebrand.[1] The heating is carried out as with the ordinary crucible but the temperature may be much higher. Removal of the sintered mass from this crucible is difficult and tedious, especially if the rock contains much iron, and this form is seldom used in the author's laboratory. We shall, then, assume that an ordinary crucible is used.

The crucible is covered and is heated over a low flame for ten or fifteen minutes, until no more vapors of ammonium chloride or ammonia are given off.[2] The bottom of the cover should be examined from time to time to see that no ammonium chloride adheres to it. A small platinum basin (p. 38) or a 30-c.c. beaker half filled with water is placed on the crucible cover, and the flame is raised until the *lower third* of the crucible is *bright red.* This heating is continued for three-quarters of an hour, a little water being added to the basin from time to time if needed,[3] and the crucible is allowed to cool.

When cold, the mass is soaked in the crucible with just enough water to cover it, and the quicklime that has been formed is allowed to slake, by which the disintegration is rendered almost complete.[1] By aid of the platinum spatula and a little water from the wash-bottle the contents of the crucible are transferred to the platinum basin, any adhering portions being removed by the spatula. A little water is allowed to remain in the crucible to soak it out. The spatula is rinsed off into the basin, which should contain not more than about 50 c.c. of water.

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[1] Hillebrand, Bull. **700.** p. 209, Fig. 20. Hillebrand–Lundell, p. 789, Fig. 39.

[2] This gentle preliminary heating is very important.

[3] This is not necessary if the crucible is placed in a square plate of fused silica, as the water will not boil.

The partially disintegrated mass is well ground up in the basin with the agate pestle, the pestle is rinsed off with a little warm water, the water in the crucible is added, and the contents of the basin are brought to a boil, which is continued gently for a few minutes. The liquid is then decanted through a 9-cm. filter into a 400-c.c. beaker.[2] The stirring-rod is rinsed off into the basin, and the mass is once more rubbed with the pestle until there are no more lumps; finally the pestle is rinsed and the basin again heated. The liquid is decanted through the filter, the powder once more heated to boiling with a little water, and finally the solid contents of the basin are brought on the filter. The basin is rinsed, and the contents of the filter are washed with hot water, in small portions at a time, the powder being well stirred up by the first additions of water from the wash-bottle.

It is impossible to ascertain when the washing is complete by acidifying drops of the filtrate with nitric acid and testing with silver nitrate, because an oxychloride of calcium is formed which dissolves slowly in water, and will thus give a reaction for chlorine long after all the alkalies are washed out. Smith states that complete washing is effected with 200 c.c. of water, but it is as well to be on the safe side and use 250 c.c., which will make complete washing certain. This volume may be conveniently marked by a thin line of paint on the 400-c.c. beaker used for this operation.

The beginner should test the thoroughness of the decomposition by dissolving a portion of the moist mass on the filter in hydrochloric acid. Solution will be complete if the fusion has been properly carried out, except, possibly, for a few black grains of ore, which will slowly dissolve in the acid.

Inasmuch as a very small amount of alkali may be retained in the cake[1] the mass in the filter may be dried and placed in the platinum basin. About one-half gram of ammonium chloride is rubbed in well and the mixture is heated and treated as before. The final filtrate is added to the first portion. The powder that adheres to the filter paper may be rejected and the washings with hot water may be few. The weight of alkali chloride so recovered is very small and the loss is negligible as a rule, if the first operation has been properly conducted, except possibly with rocks that are very high in alkalies. After having tested the matter the author does not as a rule attempt this recovery of the alkalies. add ammonia

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[1] If the rock contains much iron the cake will have been more or less fused, so that the distintegration will not be as complete as it is with most rocks. This is of no consequence, as the mass is subsequently ground up.

[2] One may advantageously use a 400-c.c. beaker of fused silica to avoid contamination by glass. One of these is shown in the frontispiece, at the extreme left.

To the filtrate a little ammonia is added and the liquid is brought to a boil.[2] About one and one-half to two grams of ammonium carbonate previously dissolved in 25 c.c. of water[3] are then added, and the boiling is continued for a minute or so. The lime is thus completely precipitated, except for a trace which is separated later, and the alkalies are left in solution as chlorides, with ammonium chloride.

The bulky precipitate of calcium carbonate is allowed to settle a little, and is then filtered through a 9-cm. filter into a capacious basin (500-c.c.). This is preferably of platinum, but as such a large one is very expensive, a gold basin can be used with equal accuracy. In default of this a fused silica or glazed porcelain basin (not a casserole) will answer, with but slight danger of contamination by alkalies taken up from the glaze. A glass basin must not be used on any account, because the liquid would be seriously contaminated with alkalies derived from it; also with a basin of pure silver it is found that silver chloride is apt to be formed.

All the precipitate is brought on the filter, the beaker is rinsed and the contents of the filter are washed with hot water in small portions at a time, until there is no chlorine reaction. The volume of liquid in the basin should be from 300 to 400 c.c. The basin is placed on the water-bath. It is best to leave it covered with a large watchglass for ten minutes, because the excess of ammonium carbonate is decomposed by the heat and the liquid effervesces. When this ceases, the cover is rinsed into the basin, and the liquid is evaporated down to dryness, *which must be complete,* as shown by the whiteness of the salts. The evaporation may be done conveniently by leaving the basin on the water-bath over night.

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[1] Mellor, p. 225; M. Dittrich, Neu. Jahrb., 1903, **1**, p. 81; M. F. Connor, Cong. Geol. Int. C. R. XII, p. 888, 1914; Hillebrand, Bull. **700**, p. 209; Hillebrand–Lundell, p. 790.

[2] Addition of ammonia is necessary to prevent the formation of soluble calcium bicarbonate. The iridescent scum on the surface of the liquid is due to the action of atmospheric CO_2 on the calcium hydroxide and chloride.

[3] The preparation of this solution should be begun when the crucible is put over the flame, so as to have the solution complete in time. It cannot be hastened by heating, because heating decomposes the ammonium carbonate.

The drying may be hastened materially by adding 5 c.c. of alcohol when the contents of the basin are almost dry, and heating to dryness on the water-bath. The salts are thus less liable to decrepitate.

The basin, covered with a dry watchglass, is then placed on a square of gauze over a low flame and gently heated. This heating must be cautious, and, if there is any decrepitation due to incomplete drying, the heating should be interrupted frequently until decrepitation subsides, or otherwise particles of the salts may be thrown up and adhere to the coverglass. If the cover is slightly dewed with moisture at first, it is well to remove it frequently and wipe the moisture off quickly, to avoid such a mishap. When decrepitation has wholly ceased and white vapors of ammonium chloride begin to rise, the cover is taken off, the wire gauze removed, and the basin is placed on the ring of the ring-support. The upper sides are gently warmed by a half-full Bunsen-burner flame, which is waved over the surface until the sides are free from ammonium chloride.

The salts at the bottom are next gently heated until no more ammonium chloride is given off. Great care must be taken that the bottom of the basin is not overheated so that the salts melt and the alkali chlorides vaporize. During this process the clear white mass becomes dark and dirty-looking, from carbonization of the traces of organic matter that even the purest ammonium carbonate usually contains. Prolonged gentle heating will cause this to disapppear to a certain extent, but as the carbon is removed by filtration, its disappearance at this stage is not necessary.

After cooling, a little water is added, just enough to dissolve the chlorides. If the rock contains sulphides, and especially if hauyne or noselite is present, a drop of dilute barium chloride solution is added to precipitate the sulphate ion, which would otherwise appear later as sodium sulphate and lead to a slight error. A few drops of the solution of ammonium carbonate are then added to precipitate the excess of barium and the small amount of lime which is always present at this stage. It is not necessary to add ammonium oxalate to the solution. After rinsing the interior as high as the salts extend, by gently rocking and tipping the small bulk of liquid, so as to insure their complete solution, the basin is placed on the water-bath and the contents are again evaporated to dryness.

Then 2 or 3 c.c. of water are poured in to dissolve the salts, and the small amount of liquid is filtered through a 5½-cm. filter placed in the 4-cm. funnel (p. 42), into a previously ignited and weighed 35-c.c. crucible. *The greatest care must be taken in pouring out the first portion of liquid,* because drops are apt to fly out of the filter if they fall from a height. The loss of a single drop at this stage would cause so relatively large a loss of the small bulk of concentrated solution as to necessitate remaking the determination from the beginning. Such loss is prevented by using a slender stirring-rod, with which a path of liquid may be streaked to the lip, having the rod wet and its end touching filter paper. The basin and filter are washed half a dozen times, preferably with warm water, and using only as little as possible, not over 3 or 4 c.c. at a time. When the washing is complete, as shown by a test for chlorine on a single drop toward the last, the crucible should not be more than three-quarters full.

A drop of very dilute hydrochloric acid may be added to the crucible, to decompose any alkali carbonate possibly present, the crucible is placed on the water-bath, and the liquid is evaporated to *complete dryness.* Care must be taken to insure this, as small amounts of water caught under the crust may long resist evaporation. It is not advisable, either here or in the evaporation in the basin, to use a platinum spatula or wire to break up the crust and hasten the operation, on account of the danger of loss of substance. The contents of the crucible can usually be rendered dry in three hours or so, if the water is kept at a brisk boil, or it may be left on the water-bath over night.

When the salts are dry, the crucible is placed on a platinum triangle, is covered, and *very gently* heated with a small flame, held in the hand and moved about at some distance below. When the slight decrepitation ceases and vapors of ammonium chloride rise, the flame is gradually raised (but not as far as the crucible bottom) until no more vapors are given off, which is ascertained by lifting the cover from time to time. The cover is then freed from ammonium chloride by heating over the flame, and the sides of the crucible are similarly treated. The salts at the bottom are then more cautiously heated with the small flame until no more vapors are given off and the salts *just begin to melt* in places. When this happens the flame *is to be removed instantly.* The bottom of the crucible should not be heated above a very faint red, scarcely visible in daylight.

It is to be remembered that the operator must, on the one hand, insure the dryness of the salts and the complete expulsion of ammonium chloride, which would later be precipitated with the potassium chloroplatinate; and on the other, avoid any vaporization of sodium or potassium chloride. This, however, need not be feared if the chlorides are not heated above their melting-points.

If more than a few drops of ammonium carbonate or oxalate have been used to precipitate the traces of lime, the salts may be darkened by deposited carbon. This will usually be burnt off entirely, or nearly so, in the process of driving off the ammonium chloride and the incipient fusion of the alkali chlorides. The slight amount of it usually remaining is practically unweighable, the author's experience has shown, and may therefore be neglected.

The platinum crucible containing the chlorides is cooled in the desiccator, weighed out quickly, and the weight is recorded as Cruc. + $NaCl$ + KCl. Then 5 or 10 c.c. of water is poured in to dissolve the salts, and if the previous operations have been properly carried out the solution will be clear, or at most only a few specks of carbonaceous matter will be present, which may be neglected as explained above. If, however, there is an insoluble residue of calcium carbonate the contents of the crucible, without addition of ammonium oxalate, must again be filtered through a small filter into another weighed crucible, the filter washed, again evaporated to dryness, and the operation repeated as before. The crucible and its now perfectly pure chlorides are weighed, and this weight and that of the new crucible are substituted for the former ones. The difference seldom amounts to more than a few tenths of a milligram.

From this point on the operations should be conducted as rapidly as possible, and the crucible, always kept covered and beneath a beaker, should not be allowed to stand longer than necessary, to avoid contamination by the ammonium chloride in the atmosphere, as pointed out by Shannon.[1]

Separation of Potash.—We now have to separate the potash and soda in order to determine each of them. For this separation there are two appropriate reagents.

The reagent that is by far the best and most used is chloroplatinic acid, which converts the alkali chlorides into chloroplatinates.[2]

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[1] E. V. Shannon, Am. Mineral., **12**, p. 411, 1927. Cf. Hillebrand–Lundell, p. 519.

[2] The term "chloroplatinate" is here adopted, instead of "platinichloride" (used in former editions) in accordance with the present usage of American and British chemists. But the author still objects to the use of the termination *-ate*, as in

Potassium chloroplatinate is practically insoluble in strong alcohol, in which the sodium salt dissolves readily. This reagent, however, suffers under the disadvantage of high cost.

The other reagent is perchloric acid, potassium perchlorate being practically insoluble, and sodium perchlorate easily soluble, in strong alcohol containing a little perchloric acid.

The perchlorate method is said to be almost, if not quite, as accurate as the chloroplatinate method. The latter will be described in detail, while the perchlorate method, which the author has never used, will be treated more briefly.

Separation as Chloroplatinate.[1]—The dried and weighed chlorides obtained as above (p. 231) are dissolved in the crucible with about 5 c.c. of water, and to this the requisite amount of a solution of chloroplatinic acid is added.

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It is necessary to add more than enough of this reagent to change the entire amount of both sodium and potassium chlorides into chloroplatinates, but any large excess is to be avoided, on account of the high cost of chloroplatinic acid, if for no other reason. We therefore use a solution of chloroplatinic acid made up to contain 0.05 gram of platinum to the cubic centimeter, as described elsewhere (p. 59). As it takes 3.36 c.c. of this to react completely with 0.1 gram of NaCl to form Na_2PtCl_6, and only 2.62 c.c. to do the same with KCl to form K_2PtCl_6, and as nearly all rocks contain both alkalies, we are sure of an excess if we assume that the chlorides are wholly sodium chloride, and calculate on this basis the amount of chloroplatinic acid solution used. The weight of the combined chlorides is therefore multiplied by 34, and the result is the number of cubic centimeters of platinum solution that is to be added.[2] If the rock is extremely rich in sodic minerals, as albite or nephelite, with little or no potash, it will be as well to take a few cubic centimeters more of the solution.[3]

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chloroplatinate and fluosilicate, for salts of these oxygen-free complex acids, because *-ate* (and *-ite*) originally indicated salts of oxygen-acids, while the ending *-ide* indicated oxygen-free salts and other compounds. In mineralogy fluosilicate means a silicate that contains fluorine as an essential constituent, not a salt of the type R_2SiF_6. The Century Dictionary recognizes this difference in usage between the two sciences.

[1] Classen, **1**, pp. 841–843, **2**, pp. 613–615; Fresenius–Cohn, pp. 245–247; Hillebrand, Bull. **700**, p. 210; Hillebrand–Lundell, pp. 518–521; Mellor, pp. 231, 234–237; Treadwell–Hall, pp. 59–64.

[2] If the chloroplatinic acid solution contains 0.10 gram of platinum in one c.c., the factor is 17 instead of 34.

[3] The calculation need be only approximate. Thus, if the chlorides weigh 0.1273 gram, we calculate $0.13 \times 34 = 4.42$ c.c., and use 5c.c. of the platinum solution.

The crucible is then placed on the water-bath and heated. If the precipitated potassium chloroplatinate does not wholly dissolve when the liquid has become warm, a few cubic centimeters of water is to be added to dissolve it. This will seldom be necessary if the directions and strengths of solutions given above are followed, even with highly potassic, leucitic rocks.

The contents of the crucible are evaporated, with occasional gentle shaking, to break up the crust as it forms, until the liquid is syrupy and the mass solidifies on cooling. This will take place when the depth of the liquid is reduced to about 2 mm., but naturally depends on the amount of alkalies in the rock. The evaporation should not be carried out to complete dryness on the water-bath.

When the evaporation is completed the crucible is removed, covered, and allowed to cool, under an unlipped beaker, to make sure that the liquid solidifies. It is then half filled with alcohol of 0.86 specific gravity,[1] contained in a small wash-bottle, and allowed to soak. During this, the Gooch crucible may be prepared with an asbestos felt as already described (p. 112), ignited, cooled, and weighed, and placed in position in the filtering flask.

By this time the disintegration of the solid mass in the crucible should be complete. If not, it may be hastened by stirring and rubbing cautiously with the lower end of a 5-c.c. pipette, the lower aperture of which should be from 1 to 2 mm. wide. When solution is complete, except for the golden-yellow crystals of potassium chloroplatinate,[2] the suction is started beneath the Gooch crucible and the fluid is transferred to it by means of the pipette. Only a little of the solution at a time is drawn into the pipette, which must never be filled as far as the bulb. The crucible with the liquid is held in the left hand close to the Gooch crucible and a little of the liquid is sucked up into the pipette and allowed to run down the sides of the filter, to avoid breaking the felt. When all the liquid has been thus decanted, a little more alcohol is poured on the precipitate in the crucible, and decanted as before into the Gooch crucible when this is empty. After three or four decantations, by which time the soluble sodium chloroplatinate is nearly gone and the liquid is almost colorless, the sides of the crucible are carefully washed down with a stream of alcohol and the pipette is rinsed both inside and out into the crucible. The bulk of the precipitate is then transferred to the filter, without the use of a rod, by a gentle stream from the alcohol wash-bottle, the depth of liquid in the crucible being so great that the drops can fall in the center without danger of breaking the felt.

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[1] If a hydrometer is not at hand an alcohol of approximately this specific gravity may be made by mixing five volumes of ordinary 95 per cent alcohol with one volume of water. Morozewicz (Bull. Acad. Sci. Cracovie, p. 796, 1906) has shown that, when Na_2PtCl_6 is present, alcohol stronger than 80 per cent decomposes the sodium salt, precipitating sodium chloride. An alcohol of less strength than 75 per cent dissolves appreciable amounts of K_2PtCl_6. (Cf. Mellor, p. 231; Hillebrand–Lundell, p. 519.)

[2] If the fluid is not yellow, or if small white grains of sodium chloride are present among the yellow crystals of K_2PtCl_6, there has not been enough platinum solution added. About 1 c.c. of this and a little water are to be added and the liquid is again evaporated nearly to dryness. According to Hillebrand–Lundell (p. 520) an orange red color indicates the presence of sodium salt.

With a slender stirring-rod, capped with a bit of fine rubber tubing, the small quantity of adhering potassium chloroplatinate is loosened and washed into the filter, the stirring-rod being also rinsed off. Owing to the bright color and the high specific gravity of the precipitate, it is easy to be sure of its complete transfer. When the crucible is again empty it is well washed, at least half a dozen times, the sides being also washed down, both inside and out. Enough alcohol may be added each time to half fill the crucible, but it must be allowed to empty before another addition. After washing for the last time, suction is continued for a few minutes to partially dry the felt.

The final drying is accomplished in an air-bath at a temperature of 130° C., which is necessary to drive off all the water. The bottom cap of the Gooch crucible is placed in position, and the crucible is covered while in the air-bath with a 7-cm. filter-paper instead of the cover. This permits evaporation, and at the same time guards against particles falling in from the top of the air-bath. The drying will usually be complete in half an hour, but it is as well after heating for this time, and having weighed the crucible, to reheat it for another fifteen minutes, or to constant weight. After cooling in the desiccator the crucible is again weighed, and recorded as Gooch + K_2PtCl_6. The weight of the potassium chloroplatinate is multiplied by 0.1938[1] to arrive at the weight of K_2O, from which is to be subtracted the amount of K_2O present in four grams of the calcium carbonate used, if this has been determined.

If a Gooch crucible is not available, the method suggested by Hillebrand for collecting the chloroplatinate may be adopted. This consists in filtering off the excess of chloroplatinic acid solution through a small (5½-cm.) filter and washing with alcohol, as little of the precipitate as possible being brought on the filter. When the precipitate has been washed free from all sodium chloroplatinate, that which is on the filter is washed into the weighed crucible by small quantities of hot water, the excess of liquid is evaporated to dryness on the water-bath, and the potassium chloroplatinate is finally dried as above at 130° C. Hillebrand prefers to use porcelain for the evaporation of the platinum solution, but for most purposes this is hardly necessary.

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[1] For a discussion of the proper factors see Mellor, pp. 233, 250.

Soda.—To determine the soda, which is done by difference, the weight of the K_2PtCl_6, however obtained, is multiplied by the factor 0.307[1] to convert it into KCl, and this weight is deducted from that of the mixed chlorides. The weight of the remaining NaCl is multiplied by the factor 0.5303 to obtain that of Na_2O, unless a correction is needed for the NaCl in the calcium carbonate. In that case the weight of NaCl in 4 grams of the calcium carbonate is to be deducted from that of the sodium chloride and the final NaCl is multiplied by 0.5303.

It is seen that the weight of Na_2O is determined by difference. But, in view of its accuracy, this method is preferable to its direct determination in the filtrate. If it is desired to do this, the filtrate is to be freed from platinum by one of the methods suggested by Hillebrand[2] and the sodium is determined as sulphate in the usual way.

Lithia.[3]—There is seldom enough lithia present in igneous rocks to warrant a quantitative determination. This would happen only with rocks high in soda and with abundant alkali feldspars or in certain pegmatites, although lithium is often present in spectroscopic traces. If it is desired to show the presence of lithium spectroscopically the filtrate from the potassium chloroplatinate is evaporated to dryness and the salts are tested with the spectroscope. There seems to be seldom theoretical reason to do even this.

To determine lithia gravimetrically the platinum is removed from the filtrate by hydrogen, as mentioned above, and the lithium is separated from the sodium and determined by the old Gooch's method, with amyl alcohol,[1] by that of Palkin, with ethyl alcohol and ether,[2] or by the use of pyridine.[3] These are described by Hillebrand-Lundell. There is little to choose between them.

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[1] The factor is more exactly 0.3067, but 0.307 will be exact enough in almost all cases. For discussion of this factor see: Hillebrand, Bull. **700**, p. 211; Hillebrand–Lundell, p. 520; Mellor, pp. 233, 250; Treadwell–Hall, p. 60.

[2] Hillebrand, Bull. **700**, p. 211; Hillebrand–Lundell, p. 520. Dr. Zies informs the author that passing hydrogen through the liquid in a flask on the steam-bath is effective and simpler.

[3] Hillebrand, Bull. **700**, p. 212; Hillebrand–Lundell, pp. 526–529; Mellor, pp. 533–535; Treadwell–Hall, p. 68.

All the platinum residues, both the chloroplatinate and the filtrates, should be preserved in a wide-mouth bottle. The platinum is recovered from time to time by the usual methods,[4] or sent to a refiner. In this way the cost of each analysis will be very small.[5]

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Separation as Perchlorate.[6]—The author has not personally used or had any experience with this method and refers the student to the authorities cited for descriptions of the procedures. He does not describe the method here because he can not recommend the perchlorate method in preference to, or as replacing, the chloroplatinate method. This for the following reasons. The latter is more accurate and more simple and rapid. Furthermore, there is always, or almost always, danger of explosions with the perchlorate method, especially in the hands of an inexpert chemist or beginner. The colleagues in the Geophysical Laboratory who have tried the perchlorate method agree in this condemnation.

Any laboratory that can not afford the initial cost of the chloroplatinic acid should not undertake the scientific analysis of rocks, especially as the cost in using this for each analysis is so small as to be negligible, if the platinum is recovered.[5]

If, for any reason, the perchlorate method is used, the author would suggest that of Smith and Ross,[7] with butyl alcohol and ethyl acetate, which does not involve the heating of organic material with perchloric acid, and which is recommended and described by Hillebrand-Lundell (pp. 523–524). Another recent method is that of G. F. Smith,[8] with butyl alcohol containing a little perchloric acid, although here it is hard to reconcile the use of such boiling alcohol with the general statement that hot mixtures of perchloric acid with any organic material are liable to explosion.

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[1] Gooch, Am. Chem. Jour., **9,** p. 85, 1887.

[2] S. Palkin, Jour. Am. Chem. Soc., **38,** p. 2326, 1916.

[3] Kahlenberg and Krauskopf, Ibid., **30,** p. 1104, 1908.

[4] Classen, **2,** p. 262; Mellor, p. 240.

[5] On the basis of about one hundred determinations of K_2O as chloroplatinate in the author's laboratory it was found that the average cost was about 7 cents for each analysis. This was chiefly the cost of recovery by the refiner; that of loss of the metal was much less.

[6] Hillebrand–Lundell, pp. 523, 533, 534; Mellor, p. 237; Treadwell–Hall, pp. 64–68; Gooch and Blake, Am. Jour. Sci., **44,** p. 381, 1917; Baxter and Kobayashi, Jour. Am. Chem. Soc., **39,** p. 249, 1917 and **42,** p. 735, 1920; Morris, Analyst, **45,** p. 349, 1920; G. F. Smith, Jour. Am. Chem. Soc., **45,** p. 2072, 1923; Smith and Ross, Jour. Am. Chem. Soc., **47,** p. 1020, 1925.

[7] Smith and Ross, Jour. Am. Chem. Soc., **47,** p. 1020, 1923.

[8] G. F. Smith, Jour. Am. Chem. Soc., **45,** p. 2072, 1923.

The insoluble potassium perchlorate ($KClO_4$) is collected in a Gooch or Munroe crucible, dried at 130° C and weighed. The factor for the conversion to K_2O is 0.3399, that for KCl is 0.5381.

A word of caution must be said as to the perchlorate method for potash. Various authorities[1] lay stress on the danger of explosions, possibly serious ones, if perchloric acid is heated with any organic material. This applies more especially to the boiling undiluted acid, or to its vapor, or to the addition of ethyl alcohol to hot perchloric acid. But there are apt to be minor explosions even with the dilute acid. Therefore, evaporations of even the dilute acid mixed with alcohol should be cautious and at as low a temperature as possible, and it is best to avoid them altogether. Purely aqueous solutions of perchloric acid and perchlorates may be evaporated without danger but, as said by Treadwell-Hall, "a bad explosion may result from heating the alcoholic solution."

Indirect Methods.—There are several indirect methods of determining the potassium and the sodium in the mixed chlorides, depending on the determination of the chlorine by either gravimetric or volumetric methods. These are dealt with in various textbooks,[2] but they will not be described here, because they are inaccurate and not suited to the analysis of rocks.

14. WATER

Do while weighing main portion

The different ways in which water, including hydroxyl, may occur in rocks have been discussed and classified at some length by Hillebrand,[3] but for the purposes of this book it is needless to do little more than to refer to him, with some slight modifications. According to Hillebrand the water in rocks is classified as: *essential* hydrogen, the presence of which is necessary for the constitution of a mineral, and *nonessential* hydrogen, the presence of which is not necessary for the constitution of a mineral, but which may be more or less adventitious. From the point of view of analysis, however, the water is referred to two groups, the *hygroscopic* and the *combined* water, the latter being the more important. These are stated in the analysis as the water expelled, respectively, below and above 105°–110° C. Although these two groups more or less overlap, they are determined by different methods, one indirect and the other direct, so that they are dealt with here in separate sections. Hygroscopic water is discussed first because the determination of it is the simpler.

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[1] Hillebrand–Lundell, p. 37; Treadwell–Hall, p. 65, notes.

[2] Blasdale, p. 46; Fresenius–Cohn, **1**, p. 2; Mellor, pp. 79, 227–231; Treadwell–Hall, pp. 2, 604.

[3] Hillebrand, Bull. **700**, pp. 64–72; Hillebrand–Lundell, pp. 676–685; Treadwell–Hall, p. 437.

Hygroscopic Water.[1]—By the term hygroscopic water is meant the water that is adsorbed by the rock powder from the atmosphere and the water may be present in microscopic cavities. Some of the more loosely combined water of crystallization of the zeolites and other hydrous minerals may also be included under this head. This "hygroscopic" water is all, or nearly all, expelled from the rock powder at temperatures of about 110° C., although Day and Allen[2] conclude from their study of feldspar powders that some of it is not expelled below 600° to 800°.

The amount of hygroscopic water in fresh rocks is usually very small; Day and Allen note that the quantities of adsorbed water determined by them "are of the same order of magnitude as those usually obtained for the water content in feldspar analyses." Notwithstanding this, it is always well to determine hygroscopic water separately from combined water. The reasons for this have been fully discussed by Hillebrand and need not be gone into here.

The influence of the fineness of the powder on the adsorption of moisture from the atmosphere, and the consequent advisability of analyzing air-dry material have already been mentioned (p. 86).

Errors.—The errors involved in the determination of hygroscopic water are negligible, especially in view of the fact that its amount in igneous rocks is always very small.

Procedure.—About one gram of the rock powder is weighed into a previously ignited and weighed platinum basin or a small platinum crucible and this is heated in an air-drying oven at a temperature a little above that of boiling water. The exact temperature is of no great importance, so long as it is about 110° C. In the U. S. Geological Survey laboratory a toluene bath is used, giving a temperature of 105° C. (Hillebrand). The author's practice is to use an ordinary copper oven, with single walls, and the flame is so adjusted as to maintain the temperature constantly at 110° C., which is readily accomplished. The basin or crucible is covered during the heating with a filter paper, the platinum cover of the crucible being removed. It will usually be found that half an hour's heating, and often less, will be sufficient to arrive at constant weight. After heating, the basin is allowed to cool in a desiccator and is weighed, heated again for a quarter of an hour, and if the weight is constant, the loss in weight, divided by the weight of the rock powder taken, gives the percentage of hygroscopic water, which should be tabulated as H_2O —.

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[1] Hillebrand, Bull. **700**, pp. 73–77; Hillebrand–Lundell, pp. 686–688; Mellor, pp. 155–157.

[2] Day and Allen, Isomorphism of the Feldspars, Carnegie Publ. **31**, p. 57, 1905.

The portion used for this determination may be used also for that of other constituents, except alkalies and ferrous oxide. Indeed, it is a saving of time if this is done. Determinations that suggest themselves are those for the main sodium carbonate fusion, for phosphorus pentoxide, for manganese, and for sulphur, baria, and zirconia.

Combined Water.[1]—Under this head is included the essential water in a rock that is chemically combined in the mineral molecules, either as hydroxyl (as in the micas), or as water of crystallization (as in analcite). With this "combined" water should be reckoned the water present in solid solution in many volcanic glasses. A small part of the two last may be expelled at 110°, but this is, in most cases, a negligible matter.

Few constituents of rocks have had the amount of time, thought, labor, and ingenuity bestowed on them that has been devoted to the accurate determination of combined water; and in all the textbooks an amount of space and attention is devoted to it that is quite disproportionate to its importance in *rock analysis.*

In the analysis of minerals, in many of which the water or hydroxyl may play a very important part in the constitution of the molecule, the accurate determination of water may be (and often is) of great importance for the correct interpretation of the composition and molecular constitution of the mineral. In fresh rocks, on the other hand, water is usually a constituent of very subsidiary importance; so that the use of any of the very complicated forms of apparatus that have been devised is quite uncalled for, unless there is some special reason for going to all the trouble and time that they involve. Even with such rocks or silicate minerals the simple Penfield method, which is capable of great accuracy, will usually be entirely adequate to the purpose.

[1] Classen, pp. 626–634; Fresenius–Cohn, **1**, pp. 72–78; Gooch, pp. 34–38; Hillebrand, Bull. **700**, pp. 77–79; Hillebrand–Lundell, pp. 690–698; Mellor, pp. 157–159, 570–575; Treadwell–Hall, pp. 438–440; L. Duparc, Bull. Soc. Franç. Min., **42**, p. 239, 1919; Penfield, Am. Jour. Sci., **48**, p. 30, 1894.

Errors.—Because of its usually minor importance in the analysis of rocks, the errors involved in the determination of water will seldom be serious.

If the water is determined by loss on ignition, a plus error will be introduced by the expulsion of other volatilizable substances such as carbon dioxide, sulphur, or chlorine. Only that of the carbon dioxide is likely to be of serious consequence. The "hygroscopic" water will, of course, also be expelled, and must be allowed for. A minus error is introduced by oxidation of any ferrous oxide present. This may be so great that, if the rock contains much ferrous oxide and but little water (as may happen with basalts, for instance), there will be a gain, instead of loss, in weight on ignition.

If the combined water is determined as loss on ignition, the oxidizing reaction of combined water on ferrous silicate or magnetite, with the possible production of hydrogen, may be taken into account.[1] This, however, is an error that may be considered as neglible.

If the water is determined by an absorption method, presence of moisture in the air used to pass through the apparatus will add to, and failure to expel or absorb all of the water will lessen, its apparent amount.

In the Penfield method the only notable source of error in general is that due to the presence of carbon dioxide in the substance. Unless this is allowed to escape from the tube containing the water, its higher specific gravity as compared with that of air will diminish the apparent weight of water. A correction may be made for it, and Penfield's paper should be consulted on this point. For fresh rocks the error does not exist or will be of no consequence.

In water determinations in rocks or minerals regard must be had for the very high temperature at which the hydroxyl is completely driven off (in the form of water) from some minerals, as with talc, topaz, chondrodite, or staurolite. For very exact determinations this point must be looked into, so that, if necessary, a sufficiently high temperature is used for complete expulsion.[2]

omit

"Loss on Ignition." [3]—The early method, and one very frequently used even at the present day, for the determination of the combined water, is that of simple ignition in a platinum crucible, on the assumption that this "loss on ignition" represents only the total water in the rock. A little consideration shows that the results in these circumstances will be accurate only if the rock contains neither substances that are easily volatilizable at the temperature of ignition (such as carbon dioxide, carbon and organic matter, sulphur, or chlorine); nor oxidizable constituents (e.g. ferrous oxide). In the former case the apparent amount of water will be too great, owing to the partial or entire loss of volatilizable ingredients; and in the latter it will be too small, on account of the gain in weight through oxidation of ferrous oxide to ferric.

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[1] Cf. R. T. Chamberlin, The Gases in Rocks, Carnegie Publ. **106**, p. 42, 1908.

[2] See Penfield, *op. cit.*, or Hillebrand, Bull. **700**, p. 78; Hillebrand–Lundell, p. 691.

[3] Hillebrand, Bull. **700**, p. 76; Hillebrand–Lundell, p. 689.

It is held by some that the error due to the latter cause may be corrected by calculation of the gain in weight which the ferrous oxide that is present in the rock, and which is separately determined, would undergo if completely oxidized to ferric oxide. This assumption, however, is by no means valid in the circumstances obtaining in the process of ignition,[1] as shown, for example, by the difficulty of completely oxidizing magnetite by ordinary ignition, even after roasting with nitric acid.

In the case of volatilizable constituents, also, there can scarcely ever be a certainty that the loss in this way will be so complete that appropriate corrections can be made with safety after their separate determination. This would be true only of carbon dioxide when derived from calcite, magnesite, or dolomite, and then only after prolonged ignition.

This being so, and it being also true that there are few rocks that do not contain such disturbing constituents (especially FeO), it follows that with most rocks the combined water should not be determined by loss on ignition.

Because, however, the determination of combined water is not always of great importance for the chemical study of rocks, this simple method may be used in certain cases. These would include very fresh igneous rocks that contain but a small amount of water, no other volatilizable ingredients, and only a small amount of ferromagnesian minerals, say up to five per cent, and consequently only one or two per cent of ferrous oxide. Many granites, porphyries, syenites, trachytes, rhyolites, andesites, and anorthosites fall under this description. For such rocks the minute error due to the very small amount of ferrous oxide present (amounting at most to one-ninth of its weight) may be deemed to be negligible, and the results of such a determination may be regarded as acceptable.

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[1] Cf. Sosman and Hostetter, Jour. Am. Chem. Soc., **38**, p. 820, 1917; Trans. Am. Inst. Min. Eng., p. 907, 1917.

If the method of "loss on ignition" is employed, the weighed crucible and its contents, which have been used for the determination of hygroscopic water,[1] are ignited (covered) at a bright-red heat for about half an hour, or to constant weight, cooled in the desiccator, and weighed. The loss in weight represents the amount of combined water. If a separate portion of powder is used for this determination, the percentage of hygroscopic water is to be subtracted from the loss in weight to arrive at that of H_2O+.

The fact must, however, be recognized that this method of procedure is not strictly accurate, and that for all high-class work, and in all rocks in which the amount of ferrous oxide is at all considerable, or if volatilizable substances are present, the combined water should be determined directly.

Use

ined H_2O + scopic H_2O

Penfield's Method.—The general inadvisability of employing any of the more complex methods spoken of above, some of which are described by the authors cited, has already been mentioned. Fortunately, a very simple and accurate method has been devised by Penfield,[2] which meets all the requirements with the great majority of rocks, needs no elaborate apparatus, and takes less than an hour for its execution. It would seem to be little known,[3] much less than it deserves to be.

This method consists in igniting the rock powder in a tube of hard glass, closed at one end and with or without a bulb in the middle, pulling off the heated end containing the powder, weighing the portion of the tube that contains the expelled water, and finally weighing this portion of the tube after drying. This gives the total amount of water, hygroscopic and combined, from which the amount of the former, as separately obtained, is to be deducted to obtain the latter. For illustrations of the apparatus used the reader is referred to the papers cited above.

It is well to list some of those accidents that are most likely to happen, and so spoil the operation, which must then be repeated from the beginning. These are: Blowing out of the powder; moving of the mass of powder into the wet zone; blowing out of the red-hot end of the tube; running of the condensed water onto the heated portion;[1] running out of the condensed water from the open end (due to too much tilt)[1]; cracking of the wet tube if a draft brings the flame in contact with the wet zone; sucking out of residual powder in the final drying.

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[1] It is not advisable to use a portion in which any other than hygroscopic water is determined, as the rock powder is apt to sinter through the great heat and be attacked with difficulty by fluxes. A separate portion should be used.

[2] S. L. Penfield, Am. Jour. Sci., **48**, p. 30, 1894. This was first used by G. J. Brush, Am. Chem. Jour., **13**, p. 110, 1891.

[3] Neither Classen, Fresenius–Cohn, Gooch, nor Morse, mention it; while Hillebrand, Hillebrand–Lundell, Mellor, and Treadwell–Hall give it but very brief description.

With most fresh igneous rocks a simple tube of rather hard glass[2] is used, closed at one end[3] and without any enlargement. The dimensions recommended by Penfield and used by the author are 0 to 25 cm. long[4] with an internal diameter of 6 mm. If the rock contains more than one half of one per cent of water it is better to have a bulb or enlargement blown about midway in the tube.[5] Indeed, this is always advisable, to guard against drops of water rolling back on the heated portion. A single bulb is sufficient for nearly all rocks, and the more complicated forms illustrated by Penfield will seldom be found to be necessary in rock analysis, although they are often necessary in the analysis of hydrated minerals.

It is important to have the tube thoroughly dry, and this "is best accomplished by heating and aspirating a current of air through it (while hot) by means of a glass tube reaching to the bottom." This should always be done, even if the tube is apparently dry. After cooling, the tube is weighed, its weight including that of the brass tube-support that is used to support it on the balance-pan.

From one-half to one gram of the rock powder is then introduced, filling the tube about two cm. from the closed end. This must be done without soiling the upper portion of the tube, and is accomplished by means of a small filling-tube, of a diameter small enough to slip easily into the open end. Such a filling-tube can be readily made from a 5-c.c. pipette by cutting the bulb in two and reducing the length of the tube to 25 cm. The filling-tube, of course, must also be thoroughly dry.[6] After the powder is introduced the tube is weighed again, to obtain the weight of the substance taken, the manipulation being gentle and delicate to avoid any rolling of the powder toward the open end.

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[1] This is not likely to happen if a bulb is present.

[2] The glass should be sufficiently hard not to droop much on heating, and yet be fusible enough to be readily pulled apart.

[3] A bulb at the end, figured by Penfield, is not necessary.

[4] The tube must not be too long to go in the balance-case, and so interfere with weighing, nor too short, in which case it would cause loss of water through lack of sufficient cooling surface and consequent heating of the cooler portion.

[5] In blowing the bulb the tube must not be bent.

[6] The filling-tube can be easily cleaned "by drawing through it a bit of cotton attached to a wire," or, if the analyst is a smoker, a fresh pipe-cleaner will answer admirably.

After a few gentle taps to form a free passage above the powder for the heated air, which might otherwise drive the powder toward the bulb and necessitate refilling and reweighing, the tube is held (not tightly) in a clamp in a horizontal position, or *very slightly sloping* toward the mouth. A narrow strip of filter paper or cloth, moistened with ice-water and kept moist and cold, is wrapped around the bulb and farther end of the tube, beyond the clamp, in order to insure condensation of the expelled water within the tube, care being taken that it is not so near to the mouth as to allow water dropped on it to enter the tube.

The closed end is then *gently heated,* the tube being tapped lightly to keep the upper passage open and prevent the mass of powder from being driven toward the open end. This is especially necessary if there is much water. After the water begins to collect in drops, the heat is gradually increased to the full heat of the Bunsen burner, but *not using a large flame.* By moving the flame along the powder, and at the same time turning the tube about its axis, the whole portion of powder is thus heated throughout to a bright red. If the end of the tube tends to sink, this is remedied by turning the tube about, the clamp having been adjusted slightly loose for this purpose. If the strip of cloth or filter paper is kept moist with cold water, and the tube is not too short, there is not any need for a screen of asbestos board, nor is it necessary to partially close the tube with a short piece of tubing drawn out to a capillary and connected by a bit of rubber tubing. It is necessary to carry on the operation in a place *free from drafts,* which might carry the flame to the moistened part of the tube, and crack it.

Toward the end it is best to substitute a Meker for the Bunsen burner. When the whole extent of the powder has been heated for at least fifteen minutes, best in small sections at a time, the tube is raised and the water is very cautiously and gently driven to a safe distance beyond the powder and toward the open end or into the bulb. This must be done with a small flame and without causing the water to boil and without cracking the tube.

With the *tip of the Meker flame* a narrow zone of the tube, well beyond the powder, but not near the water, is heated to softness, the tube being turned, and the end containing the powder is drawn off gently with the brass tongs,[1] the tips of which have been slightly warmed (not to redness) in a nearby Bunsen flame. The narrow connection is sealed off and the end containing the powder is rejected. It is important that none of the powder be left above the sealed-off end, as it might be sucked out during the subsequent aspiration.

The remaining portion of the tube containing the water is allowed to cool in a horizontal position and with the strip of paper or cloth kept cold. It is wiped clean and dry on the outside and weighed. It is then replaced in the clamp and gently heated, the moist air and steam being sucked out by means of a small tube extending an inch or so, and connected with the suction-pump. After thorough drying in this way it is allowed to cool and is again weighed.

The loss in weight is the amount of total water, which is reduced to percentage figures by division by the amount of substance taken; the percentage of hygroscopic water already determined is then subtracted.

In nearly all cases the simple method described above will yield very accurate results. But when rocks, as some metamorphic ones, contain minerals such as talc, topaz, chondrodite, or staurolite, the water of which is not completely driven off except over a blast, it becomes necessary to use a more intense method of heating. For a description of this, reference may be made to Penfield's article.

A narrow ring, or rings,[2] of sodium chloride or sodium sulphate is sometimes seen in the dry tube. It is caused by the presence of chlorine or sulphur in the rock. Such rings may be tested for these anions by dissolving them in a little water and adding silver nitrate and barium chloride to separate drops. In the usual rock analysis it is scarcely necessary to fix the chlorine and sulphur during the ignition by lime or other retainers, as Penfield recommends.

If there is much CO_2, the correction for it, described by Penfield, may be applied; in most cases it is not needed.

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16. PHOSPHORUS PENTOXIDE[3]

Phosphorus pentoxide is best determined in a separate portion of rock powder. The operation consists in decomposing the rock powder with nitric and hydrofluoric acids, rendering the remaining silica insoluble by heating, and determining the phosphorus pentoxide in the residue as magnesium pyrophosphate.

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[1] Ordinary brass tongs should be used for this. Platinum-tipped or chromel tongs should not be used because they are apt to adhere to the hot glass.

[2] The farther ring is of chloride, the nearer of sulphate.

[3] Classen, **2**, pp. 564–570; Fresenius-Cohn, **1**, pp. 446–447; Gooch, pp. 81–82; Hillebrand, Bull. **700**, pp. 177–179; Hillebrand-Lundell, 560–566, 757–758; Mellor, pp. 590–598; Treadwell-Hall, pp. 380–384.

Errors.—The chief error to which the determination of phosphorus pentoxide may be subject is caused by the somewhat uncertain composition of the ammonium magnesium phosphate precipitate, which varies according to the conditions that obtain during precipitation. It is not necessary to go into the matter here, as it has been discussed on p. 206 in describing the determination of magnesia.

Mellor[1] states that the presence of titanium retards the precipitation of ammonium phosphomolybdate. This is not mentioned by the very careful Hillebrand, and in any case its influence would be negligible for the very small amounts of P_2O_5 present in igneous rocks. Hillebrand states that P_2O_5 should not be determined in the solution obtained from the pyrosulphate fusion, as was suggested in the last edition, if the material is scanty. He gives a method to be used in this case, based on a paper by Chatard.[2]

Fortunately, the amount of phosphorus in igneous rocks is generally so small that errors in its determination are of little importance.

If considerable vanadium is present in the rock—a very rare occurrence, the percentage of V_2O_5 is to be subtracted from that of P_2O_5, as the vanadium is precipitated as vanadomolybdate along with the phosphomolybdate and weighed as magnesium pyrovanadate[3] with the magnesium pyrophosphate, if phosphorus is present in much greater quantity than the vanadium, as it invariably is in rocks.

It is essential that the amount of ammonium molybdate be in large excess. The quantities of solution suggested later suffice for the great majority of rocks, in which the percentage of P_2O_5 is less than 0.5. Exceptionally large amounts will be detected by the precaution of adding more molybdate solution to the filtrate and allowing it to stand.[4]

Precipitation as Phosphomolybdate.—The phosphorus pentoxide is best separated from the other constituents present in the solution by the old and well-known method of precipitation as phosphomolybdate. The conditions recommended for this vary considerably, but the author has found the following procedure to be the best and most rapid.

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[1] Mellor, p. 594.

[2] T. M. Chatard, Bull. **78**, p. 87, 1891.

[3] Cain and Hostetter, Tech. Pap. Bur. Standards, No. **8**, 1912.

[4] It is in such cases that the microscopic examination of a thin section may be especially useful, showing the presence of abundant apatite.

For the decomposition, about one gram of rock powder is weighed out into a small platinum basin, or, if that is not available, into a capacious crucible. The rock powder is mixed with 10 c.c. of water, taking the precaution to prevent loss of powder noted previously, and is stirred up with a small platinum spatula or stout platinum wire, which is left in the basin for stirring. Then 5 c.c. of concentrated nitric acid is added; about 2 c.c. of hydrofluoric acid is next poured in; and the mixture is evaporated to dryness on the water-bath with occasional stirring. Evaporation with small quantities of nitric acid alone is repeated twice, to decompose the fluorides as completely as possible.

It is well to add a few drops of strong solution of ammonium nitrate before the final evaporation to dryness, because this aids in driving off the hydrofluoric acid.[1]

When completely dry after the last evaporation, the basin is heated until the contents become brown, and when cool the crust is moistened with 10 c.c. of a mixture of nitric acid diluted with four times its volume of water, and the liquid is gently boiled for a few minutes, to convert any metaphosphate or pyrophosphate, possibly produced by heating, into orthophosphate. Solution will be complete, except for silica, insoluble sulphates, and fluorides. The liquid is then filtered through a 5½-cm. filter into a 250-c.c. beaker. The basin is to be rinsed and the filter washed half a dozen times with the same warm dilute acid. The volume of the liquid should not be more than about 50 c.c. [illegible] #/ + filter

About 25 c.c. of ammonium nitrate solution (containing 340 grams of ammonium nitrate to the liter) is added,[2] and the liquid is heated to boiling. Then a *hot* mixture of about 20 c.c. each of ammonium molybdate solution (p. 57) and of dilute nitric acid[3] (sp. gr. 1.153) is added. This is best done by pouring in a thin stream, while the hot liquid is kept in constant rotation. Precipitation should be immediate and complete, but it is well to let the liquid stand (covered) for a few hours. [illegible] 11/21 Yellow ppt.

The liquid is then filtered through another 5½-cm. filter, the bright yellow precipitate being disturbed as little as possible. The latter is washed with a mixture of weak solution of ammonium nitrate, nitric acid, and water, in equal parts, washing down the sides of the beaker until the addition of ammonia water in excess produces no permanent precipitate in a few drops of the filtrate in a watchglass. About 50 c.c. of the washing mixture will usually be ample, and it should be prepared in a small beaker when needed. P_2O_5

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[1] E. S. Shepherd, personal communication.

[2] Hillebrand–Lundell (p. 758) suggest adding 1-2 grams of boric acid to convert any hydrofluoric acid to fluoborate (p. 561). This is not necessary.

[3] A mixture of 150 c.c. of nitric acid and 450 c.c. of water.

Although the amounts of ammonium molybdate solution are ample for most igneous rocks, yet it is a wise precaution to add another 20 c.c. of molybdate solution to the filtrate.[1]

If a yellow precipitate forms on standing for an hour or two, 10 c.c. more of the molybdate solution is added and the precipitate is filtered off after standing another hour. This, of course, is treated in the same way as the original precipitate and the resulting solutions are mixed for the precipitation of the ammonium magnesium phosphate.

All the phosphorus is now in the precipitate of ammonium phosphomolybdate and the beaker containing the greater part of this is placed beneath the funnel. The filter is then filled with ammonia diluted with an equal amount of water, which dissolves the small portion of precipitate in the filter and part or the whole of that in the beaker, assisted by stirring. If solution is not complete, more ammonia must be added. The filter is then washed, a half dozen fillings with water being sufficient.[2] here dissolving yellow ppt.

To the solution in the beaker, which may amount to 100 c.c., 10 c.c. of "magnesia mixture," is added,[3] best through the same filter, to remove any possible deposit in the "magnesia mixture." The beaker is allowed to stand for twelve hours, or overnight. The contents are then filtered through a small paper filter and the precipitate is collected on the latter, that adhering to the sides of the beaker being

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[1] Mellor (p. 596) gives the following table for the relative volumes appropriate for various weights of P_2O_5.

P_2O_5, gram	Ammonium Molybdate, c.c.	$(NH_4)NO_3$, c.c.	HNO_3, c.c.
0.01	15	20	10
0.005	15	20	10
0.002	10	15	5

[2] If it has been necessary to precipitate more phosphorus in the previous filtrate the two solutions of phosphomolybdate are, of course, mixed and precipitated as above.

[3] If there is much phosphorus more magnesia mixture should be added. At least 1 c.c. of magnesia mixture is needed for each centigram of phosphorus pentoxide in the solution. Methyl-red should be added, to ensure a proper excess of ammonia, if the acidified magnesia mixture is used.

rubbed off and collected in the filter. The precipitate of ammonium magnesium phosphate and the filter are well washed with weak ammonia water.

The filter with its contents is placed in a small weighed platinum crucible, and, after the filter has been carbonized, the crucible is ignited at a bright-red heat. When cool, the crucible and contents are weighed, and the weight of the $Mg_2P_2O_7$ is multiplied by 0.638 to reduce it to P_2O_5. The appropriate weight of P_2O_5 determined from this percentage is to be deducted from the weight of the precipitate by ammonia (p. 179), to arrive at the correct weight of alumina.

The phosphorus may also be determined, more rapidly and about as accurately, as phosphomolybdic anhydride by Woy's method.[1] For this procedure the yellow phosphomolybdate precipitate is collected in a weighed Gooch crucible and washed with a mixture of the ammonium nitrate solution and dilute nitric acid, about 50 c.c. being usually sufficient. The lower cap of the Gooch crucible is then put on, and the crucible is gently heated until the contents are dry and no more vapors of ammonia or ammonium salts arise. The heat is then raised until the bottom is a dull red, which is continued until the yellow mass is entirely decomposed into greenish-black anhydride, $24\ MoO_3.P_2O_5$. About ten minutes will suffice for this. The weight of the anhydride multiplied by 0.04 (for the usual small amounts) gives the weight of P_2O_5. According to the author's experience the method is rapid, accurate, and satisfactory.

17. MANGANOUS OXIDE[2]

Manganous oxide is best determined in a separate portion by a colorimetric method, which is very accurate and serves admirably for the small amounts (usually less than 0.5 per cent) that are almost invariably found in igneous rocks. If the manganous oxide amounts to one per cent or more, as it may in some silicate minerals or in very exceptional rocks, it may be separated by the basic acetate method (p. 175) and determined gravimetrically. The procedure is described later. Or it may be precipitated with alumina by bromine (p. 170), and determined colorimetrically. This is usually the better.

Errors.—There are no serious errors inherent in the colorimetric method if the solution is properly and completely oxidized to permanganate, which can readily be accomplished.

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[1] Woy, Chem. Ztg., **21**, p. 422; Hillebrand-Lundell, p. 560; Treadwell-Hall, p. 383.

[2] Hillebrand, Bull. **700**, pp. 134–138; Hillebrand-Lundell, pp. 350, 743; Mellor, pp. 371–382; Treadwell-Hall, p. 134; Yoe, Colorimetry, pp. 271–281.

The great liability to error involved in the basic acetate method has already been discussed with alumina (p. 167). The error here, through weighing of alumina with the manganous oxide, may easily amount to many times the weight of the manganous oxide present. For this reason the high figures often reported for manganous oxide in rock analyses are regarded with more than suspicion.[1]

If the manganous oxide is not separated and determined, some of that present will be precipitated with and appear as alumina, probably because it is peroxidized. A smaller portion falls with the lime, and the rest—generally the largest portion—is precipitated with the magnesia.[2] As the amount of manganous oxide in igneous rocks is very small, seldom over 0.50 and usually under 0.20 per cent, this error will not be serious for the great majority of rocks.

Colorimetric Methods.[3]—The colorimetric methods for the determination of manganese are based on the ready oxidizability of manganese solutions to purple permanganate, the depth of color of which varies the concentration. This oxidation may be accomplished by several reagents, among which lead dioxide, sodium bismuthate, and ammonium persulphate have been employed and are the best known. The first two are disadvantageous because the excess lead oxide and bismuthate must be filtered off; while the persulphate needs the presence of silver nitrate as a catalyzer, which renders the procedure somewhat uncertain, as will be seen.

Use of Periodate.—Recently Willard and Greathouse[4] have suggested the use of a periodate as an oxidizing agent. This method "is free from all the faults of other methods, and yields results of a high degree of accuracy,"[5] and it is the only one that the author as well as all the other chemists in the Geophysical Laboratory now use. Because the reagent may be somewhat difficult to procure, the persulphate method will also be described.

The color produced by periodate is much more stable than that produced by persulphate, remaining unchanged for several months.[1] The use of periodate also avoids the annoyingly erratic behavior that often attends the use of silver nitrate in the persulphate method. The high cost of the periodate is offset by the very small quantity needed for each determination of manganese.

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[1] Cf. H. S. Washington, Prof. Paper **99**, pp. 17, 20, 21; Hillebrand, et al., Jour. Am. Chem. Soc., **28**, p. 233, 1906; E. V. Shannon, Jour. Washington Acad. Sci., **17**, p. 451, 1927.

[2] Hillebrand, Bull. **700**, p. 134; Hillebrand–Lundell, p. 741.

[3] For references see page 249.

[4] H. H. Willard and L. H. Greathouse, Jour. Am. Chem. Soc., **38**, pp. 2366–2377, 1917.

[5] The occasional variation in tint arising from the carbon in steels (Yoe, Colorimetry, p. 275) is, of course, not met with in the analysis of rocks.

Start About one gram of the rock powder is weighed out into a capacious platinum crucible, or better, a small platinum basin, and 10 c.c. of sulphuric acid (1:1) and 5 c.c. of hydrofluoric acid are poured in. After a thorough mixing with a small platinum spatula or wire, the mixture is heated gently until the powder is wholly decomposed and then more strongly until white fumes of SO_3 are given off. After cooling, 5 c.c. of dilute sulphuric acid is added and the heating is repeated, this being done once or twice more to insure the expulsion of the hydrofluoric acid. The last time it is best to heat almost to dryness. The insoluble residue is filtered off through a small filter and washed with small portions of hot water, the filtrate and washings being caught in a 200-c.c. Erlenmeyer flask. They should amount to about 100 c.c. — To here 11/25/55 ←

At least 10 to 15 c.c. of concentrated sulphuric acid is poured in,[2] and 0.2 to 0.4 gram[3] 25 of solid potassium periodate is added. The solution is boiled for a minute, kept hot for five or ten minutes, and then cooled. The purple color begins to appear on heating, and attains its maximum on cooling. It is then transferred to a stoppered 250 ~~200~~-c.c. measuring flask and filled to the mark. The final test solution should not contain more than 0.001 gram of MnO per 50 c.c., otherwise it will be too dark.

By means of a 10-c.c. pipette, 10, 20, or 30 c.c. of the standard manganese solution (p. 68) is transferred to a 150-c.c. beaker, diluted with a little water, and is treated with sulphuric acid and periodate, exactly as with the test liquid. The amount to be treated will depend on the depth of color of the test solution. Our usage is to have the test solution darker than the standard, but this is optional and immaterial, as in the case of titania.

The colorimetric comparison is carried out exactly as was done in the determination of titania (p. 192). It is decidedly more easy to match the colors of permanganate solutions than those of titanium. The calculations needed follow the lines laid down for titania.

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[1] The author has kept a test solution for more than six months without perceptible change of color, even though it was exposed to direct sunlight during part of the day. The colored standard solution may be used with safety for several months.

[2] Instead of this, 20 c.c. of nitric acid may be added.

[3] A large pinch will usually suffice.

Standard soln. from
7 mg. MnO [illegible] c.c.

Use of Persulphate.—The use of persulphate is described, in spite of its defects, because it may be difficult to obtain the periodate. The rock powder is decomposed by evaporation with sulphuric and hydrofluoric acids as has been described above (p. 251). The filtered solution is contained in a 200-c.c. Erlenmeyer flask.

Inasmuch as the color of the permanganate produced by persulphate is not very stable, it is well to oxidize to permanganate in batches of three or four rocks, the clear filtrates being preserved (in covered flasks) for this purpose.

To the clear rock solution 10 c.c. or more of silver nitrate solution[1] is added for each milligram, or 0.01 per cent of the manganese present in the rock. For very siliceous rocks, such as granites or rhyolites, 10 c.c. will be ample, but for most rocks 20 or 30 c.c. should be used. It is essential to have an excess of silver nitrate, and the author therefore prefers a solution containing 3, rather than 2, grams to the liter.

If there is a precipitate of silver chloride, which will happen if the rock contains sodalite or scapolite, the liquid is to be boiled and well stirred to coagulate the precipitate, and is filtered into another small flask, the filter being washed two or three times with a little water.

Then 10 c.c. of dilute (1:1) sulphuric acid is poured in, about 2 grams of solid ammonium persulphate is added, and the flask is gently heated over a low flame until the contents begin to boil. The salt dissolves with a crackling noise, and as the liquid warms, the purple color of the permanganate appears, which gradually deepens until it attains a maximum. Soon after the color begins to appear, it is well to remove the flask from the flame and place it in a basin containing cold water, or to hold it under the cap until the color has reached its greatest depth.

With some rocks, or under certain conditions, the color of the liquid is a peculiar red, due possibly to the formation of manganic salts. If sufficient silver nitrate is present this will gradually change into the true purple of permanganate solutions. But to hasten the process, the solution may be decolorized by cautiously adding a few drops of a solution of sulphur dioxide. To the resultant, 5 or 10 c.c. of silver nitrate solution and one gram of persulphate are added. The proper color will now appear on heating.

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[1] This acts as a catalyzer and its presence is essential to the reaction.

Sometimes, after the proper coloration has begun at the bottom, the rest of the liquid assumes a dirty brown color, due to the separation of manganese dioxide. This may be caused by insufficient silver nitrate, but it is generally due to insufficient sulphuric acid. In this case the liquid is cleared and decolorized by the cautious addition of sulphur dioxide; 10 c.c. of dilute sulphuric acid and 5 c.c. of silver nitrate and about one gram of persulphate are added and the solution is brought to a boil. Sufficient sulphuric acid should always be added at the beginning to prevent this annoying discoloration, the rectification of which will add considerably to the volume of the liquid.

When the proper color has been obtained and the liquid has cooled to room temperature, the solution is poured into a 200-c.c. measuring flask, with stopper, unless the rock contains much manganese, when a 250-c.c. flask is to be used.

The depth of color should be considerably different from that of the standard, so it is well not to dilute the test solution until the standard has been prepared.

The standard solution is prepared as before, except that persulphate and silver nitrate are used, instead of periodate.

The colorimetric comparison is carried out as in the periodate method or that for titania.

If bromine or persulphate has been added prior to the precipitation with ammonia (p. 169) the weight of the manganese, calculated as Mn_3O_4 by multiplying the weight of MnO by 1.075, is to be subtracted from that of the ignited ammonia precipitate. Otherwise the amount of MnO is to be assumed to be distributed between the Al_2O_3, CaO, and MgO.

Gravimetric Method.—If the basic acetate method has been used, and it is desired to determine manganese in the main portion, it may be done according to the following method described by Hillebrand[1] and used by him in cases to which the colorimetric method is not applicable. For the reasons given on p. 167, this gravimetric determination should not be used unless the analyst is forced to do so.

The combined filtrates from the precipitate of alumina, iron, etc., if the basic acetate method has been used, are evaporated down to a bulk of about 100 c.c., best in the platinum basin, after ammonia has been added to alkaline reaction. This will in almost all cases produce a precipitate of aluminum and ferric hydroxides, which must be filtered off on a small filter, ignited, and weighed. It is at this point that there is danger of neglecting to collect the small precipitate of alumina, if the manganese is precipitated without previous filtration, so that any alumina or iron oxide present is weighed with it. This is one cause of the inordinately high figures for manganese shown by many rock analyses.

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[1] Hillebrand, Bull. **700**, p. 136; Hillebrand–Lundell, p. 742.

The filtrate is caught in a 200-c.c. Erlenmeyer flask, and if the platinum basin is stained brown by deposited manganese, this is to be dissolved in a few drops of hydrochloric acid and a drop of sulphurous acid and washed into the flask.

Enough ammonia is added to make the contents of the flask strongly alkaline, and a current of H_2S is passed through it for ten minutes, which precipitates the manganese, and also nickel, cobalt, copper, zinc, and the platinum which may have been derived from the basin. The flask is corked and allowed to stand for twenty-four hours.

The precipitated sulphides are collected on a 7-cm. filter, and washed with water containing a little ammonium chloride and ammonium sulphide, the flask being also rinsed with this. The filtrate is received in a 400-c.c. beaker, and reserved for the determination of lime and magnesia (p. 201).

The sulphide of manganese (and zinc) is dissolved by passing a few cubic centimeters of hydrogen-sulphide water acidified with one-fifth of its bulk of hydrochloric acid through the filter, and the filter is washed several times. The liquid is received in a small porcelain or platinum basin and evaporated to dryness. A few drops of solution of sodium carbonate are added and the contents of the dish are again evaporated to destroy ammonium salts, which would hinder the complete precipitation of manganese. The dry salts are then dissolved in about 10 c.c. of water to which a few drops of hydrochloric acid are added, and are precipitated with sodium carbonate. The manganese carbonate is collected on a 5½-cm. filter, washed, ignited in a weighed crucible and weighed as Mn_3O_4.

The black residue on the filter may contain nickel, cobalt, copper, and platinum. The filter is incinerated in a porcelain crucible, and the residue is dissolved in a few drops of aqua regia, evaporated to dryness in the crucible, dissolved in a little water and hydrochloric acid, and a little strong hydrogen-sulphide water is added, which will precipitate the copper and platinum. These are filtered off on a small filter, and in the filtrate, to which ammonia is added, nickel and cobalt are precipitated by hydrogen sulphide. A few drops of acetic acid are added and the liquid is allowed to stand for some hours, when the nickel (and cobalt) sulphides are caught on a 5½-cm. filter, ignited, and weighed as oxide. The amount of cobalt is so small in terrestrial rocks that it is not necessary to separate it from the nickel, but its presence may be established, if desired, by testing the oxide with the borax bead.

It is, however, always best to determine nickel and copper in a separate portion of the rock powder, as described on p. 270.

[illegible] to 259

18. Total Sulphur, Zirconia, Baria, and Rare Earths

These constituents may be determined in separate portions, but it is a great economy of time to determine them in the same portion by the following plan, which was first published by Hillebrand,[1] and independently worked out by the author. The whole process, although apparently complicated, in reality takes very little extra time for its execution, as the volumes of liquid are small, and the various operations may be carried out during pauses between the main determinations, when solutions are being evaporated, etc.

Decomposition.—For this set of determinations one gram of rock powder is sufficient.[2] About this amount is weighed out into a weighed platinum crucible, mixed with four or five times its weight of sodium carbonate, and the mixture is fused precisely as has been described above (p. 148).

If pyrite is present a small pinch of powdered potassium nitrate is mixed with the carbonate,[3] which should have been tested to see that it is free from sulphur or sulphates. If much niter is used the crucible will probably be attacked. The reaction between the nitrate and the carbonates gives rise to considerable effervescence, and the fusion should therefore be carried out cautiously and at as low a temperature as possible, until all nitrous fumes have disappeared. The temperature may then be raised and the operation carried out as above.

When the cake is perfectly cold it is detached from the crucible and thoroughly leached with water, until all soluble matter is dissolved; a drop or two of alcohol is added to reduce any sodium manganate that may be present. The leaching is best done in the platinum basin, the cake being crushed with the agate pestle.

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[1] Hillebrand, Bull. **176**, p. 73; see Bull. **700**, pp. 170–172; Hillebrand–Lundell, pp. 750–756.

[2] If the rare earths are to be looked for, two grams should be taken. In this case eight grams of sodium carbonate are to be used for the fusion.

[3] This is seldom necessary or advisable.

Of the constituents that immediately concern us, the sulphur (that as sulphide as well as that as sulphate) passes into solution as sodium sulphate, while the baria and zirconia remain undissolved, the former as barium carbonate and the latter as sodium zirconate. The rare earths are insoluble.

Sulphur.—The liquid is filtered through a 7-cm. filter, as little as possible of the undissolved residue being brought on this, and the residue and filter are well washed with a very dilute solution of sodium carbonate to prevent turbid washings (Hillebrand). The further treatment of the residue will be found later under Zirconia (p. 257).

If the filtrate is yellow the presence of chromium is indicated and it may be determined either in this liquid, or in a separate portion, by a colorimetric method, as described on p. 269. In most rocks the filtrate is colorless, when the absence of chromium may be noted in the tabulation of the analysis, and this constituent need not be looked for. Assuming that it is absent, or even when it is present,[1] we may proceed to the determination of sulphur in this liquid.

The filtrate, which should amount to 150 to 250 c.c., in a 400-c.c. beaker, is colored with two or three drops of methyl orange solution, and hydrochloric acid is added gradually through a small funnel with curved tip, the beaker being covered to prevent loss, until the original yellow color changes to pink, indicating that the liquid is acid. About a half gram, or at most one gram, of barium chloride dissolved in 25 c.c. of water is added to the boiling liquid, the cover and sides are washed down, and the beaker is allowed to stand until the barium sulphate has settled.[2] There is little danger of silica contaminating the barium sulphate, in the bulk of liquid recommended above, but if this should happen it is removed later. It is obvious that failure of barium chloride to produce a precipitate indicates the absence not only of sulphur, but of SO_3. In this case the sulphate need not be looked for, but both may be stated in the tabulation as absent.

The liquid is filtered, all the barium sulphate being brought on a small filter (7-cm.) by means of a rubber-tipped rod, and the wash-bottle; the filter is then well washed. The filter is ignited in a small weighed crucible,[1] the barium sulphate evaporated with a few drops of hydrofluoric acid and one of sulphuric acid to expel any silica possibly present, and again ignited and weighed.

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[1] The colorimetric determination of chromium, if it is done here, must precede the determination of sulphur.

[2] If very little sulphur is present, the barium sulphate precipitate is rendered easily visible by gently rotating the liquid with the rod and allowing it to stand.

For the very small amounts of sulphur present in most igneous rocks the precautions and refinements that have been suggested[2] in the precipitation of barium sulphate to insure its purity, are not necessary.

The weight of the barium sulphate is multiplied by the factor 0.137 to convert it to sulphur. If SO_3 is present in the rock and this has been determined in another portion (p. 261), the factor 0.343 is used to convert the $BaSO_4$ to SO_3 and the appropriate weight of SO_3 already determined is subtracted from this. Unless, however, haüyne or some other SO_3-bearing mineral is present, it is best to calculate all the sulphur as S and state it thus in reporting the analysis.

Zirconia.[3]—All of the zirconia in the rock is present as sodium zirconate in the residue insoluble in water, which therefore serves for the determination of this constituent. This is best done by precipitation as phosphate, in a solution containing a large excess of the precipitant.

This precipitation was formerly made[4] in a solution containing but little sulphuric acid, and using a very small quantity of phosphate as precipitant. In recent years, however, it has been found that these conditions lead to erroneous results, either because of incomplete precipitation or precipitation of zirconium phosphate of variable composition, or both. Zirconia, therefore, is always to be determined by the excellent method worked out by Lundell and Knowles.[5]

The errors are negligible.

The part of the residue that adheres to the filter (p. 256) is washed back into the beaker containing the bulk of the residue, by

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[1] The paper should be carbonized slowly and at a low temperature and the carbon burnt off cautiously, to avoid loss. Cf. Hillebrand–Lundell, p. 577. These precautions apply especially to large amounts of barium sulphate.

[2] Allen and Johnston, Jour. Am. Chem. Soc., **32**, p. 588, 1910; Johnston and Adams, Jour. Am. Chem. Soc., **33**, p. 829, 1911. Cf. Hillebrand–Lundell, p. 575.

[3] Hillebrand, Bull. **148**, p. 48, 1897; Bull. **700**, pp. 172–176; Hillebrand–Lundell, pp. 446–448, 752–755; Mellor, pp. 495–498; Treadwell–Hall, p. 123. Schoeller-Powell, (p. 101), describe other methods for the determination of zirconium.

[4] Hillebrand, Bull. **422**, p. 141; Bull. **700**, p. 173; H. S. Washington, Manual, 3rd edition, p. 227.

[5] Lundell and Knowles, Jour. Am. Chem. Soc., **41**, p. 1801, 1918.

holding the funnel sidewise and directing a strong stream of water from the wash-bottle against all parts of the filter, the liquid dropping into the beaker beneath. With care, and if done while the residue is still moist, the removal can easily be made practically complete. It is of no consequence if a little adheres to the filter.

This insoluble residue contains not only all the zirconia but all the baria (as carbonate) of the rock, with carbonates of lime and magnesia, and possibly a little silica. To the contents of the beaker, containing about 50 c.c. of liquid, is added about 2 c.c. of sulphuric acid, the beaker being covered to prevent loss by effervescence. On gentle warming almost all of the residue dissolves, the baria remaining as sulphate. The small insoluble residue is filtered into a 250-c.c. beaker, and is reserved for the determination of baria (p. 259).

To the filtrate, which now contains all the zirconia as sulphate, is added 15–20 per cent by weight (9 per cent by volume) of concentrated sulphuric acid. The titanium present is oxidized and *kept in solution* by the addition of 5 c.c. of hydrogen peroxide. This colors the liquid yellow, but this liquid cannot be used for the colorimetric determination of titanium because of the bleaching effect of the phosphate subsequently added.

Any soluble alkali phosphate may serve as a precipitant. Lundell and Knowles used secondary ammonium phosphate, but microcosmic salt answers equally well. About one gram of microcosmic salt is dissolved in 10 c.c. of water, and this, (filtered if necessary) is added to the yellow liquid, which may be either cold, or (preferably) at 40° to 50° C. The liquid is allowed to stand for at least six hours, or best overnight. It is then filtered through a small filter, decanting as much of the liquid as possible to avoid clogging the filter. The precipitate is well washed with cold 5 per cent solution of ammonium nitrate, to prevent the hydrolysis of the zirconium phosphate, which takes place if water alone is used. The filtrate is reserved for the determination of the rare earths (p. 260).

The filter and precipitate are ignited in a small platinum crucible, the cover being left slightly open. The ignition should be cautious and over a low flame until the carbon is destroyed, when it is heated for ten to fifteen minutes over a Meker burner. It is weighed as ZrP_2O_7, of which the factor for reduction to ZrO_2 is 0.432, or 0.43 for the small amounts usually found. This is to be subtracted from the weight of the ignited ammonia precipitate.

The zirconium phosphate, as thus obtained, is free from titanium, iron, and aluminum. "If there is reason to think that the precipitate is not pure, the weighed phosphate is fused with a little sodium carbonate and the cake is leached with water. The insoluble matter is collected on a filter, washed, ignited, and fused with potassium pyrosulphate. The melt is dissolved in sulphuric acid of 20 per cent strength, and the precipitation with alkali phosphate repeated" (Hillebrand).

If it is desired to verify the zirconium qualitatively this may be done by testing the solution of the insoluble residue from the leached carbonate fusion with turmeric paper (Hillebrand). A still more delicate test for zirconium is sodium alizarinsulphonate, suggested by de Boer.[1] This gives a characteristic pink color with zirconium in the presence of strong hydrochloric acid, the pink changing to yellow on addition of a soluble fluoride. Phosphoric acid interferes with the reaction, this test must therefore be carried out on the leached cake from the sodium carbonate fusion.[2]

Baria.[3]—The residue left on solution of the zirconia in dilute sulphuric acid contains all the baria, with traces of strontia and often some lime, as insoluble sulphates. To bring these into solution it is collected on a small filter, as described above, the filter and contents are ignited in a small crucible and fused with about one gram of sodium carbonate, the fusion being continued for ten to fifteen minutes to permit the complete conversion of the barium sulphate into carbonate. There should be enough carbonate for this conversion by mass action. here (fusion)

The cake is leached with warm water, which may be done in the crucible, filtered through a small filter, and well washed. After a fresh 250-c.c. beaker has been placed beneath the funnel, the carbonates are dissolved on the filter in a very little warm, dilute (1:5) hydrochloric acid, and the filter is well washed. The liquid in the beaker is made up to at least 150 c.c. to prevent precipitation of strontium and calcium sulphates, and 2 c.c. of concentrated sulphuric acid is added. After standing for twenty-four hours, the precipitated barium sulphate is filtered off, ignited, and weighed. It will seldom be necessary to purify it by repetition for contamination by calcium or strontium. Multiplication of the weight of $BaSO_4$ by 0.66 reduces it to BaO.

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[1] J. H. de Boer, Rec. Trav. Chim. Pays-Bas, **44**, p. 1071, 1925.

[2] The author is indebted to Dr. E. S. Shepherd for this information.

[3] Hillebrand, Bull. **700**, p. 170; Hillebrand-Lundell, pp. 504, 750-752; Mellor, p. 517; Treadwell-Hall, p. 424.

Rare Earths.[1]—In the case of rocks that are high in soda it may be of interest to determine the rare earths, oxides of the metals of the cerium and yttrium groups, as these oxides often occur in such rocks in weighable amounts. This may be carried out by the simple method devised by Hillebrand,[2] which is sufficiently accurate for the small amounts that are present in rocks. If the total percentage of the rare earths is several tenths of one per cent it may be well to separate them into the earths of the cerium and yttrium groups. This will seldom be called for, even in highly sodic rocks.

For the determination of the rare earths it is most convenient to use the acid filtrate from the precipitate of zirconium phosphate, inasmuch as zirconium should always be determined if the composition of the rock warrants the search for the rare earths, because both are found together in relatively largest (though usually absolutely small) amounts in highly sodic rocks.[3]

The filtrate from the zirconium phosphate is precipitated with a solution of potassium or sodium hydroxide in decided but not too great an excess. This will keep the alumina in solution, but will precipitate the rare earths along with the ferric oxide and titania. The precipitate is washed several times with hot water, brought on a 9– or 11–cm. filter where it is again washed two or three times.

It is then washed by a jet from the wash-bottle into a small platinum basin, a few cubic centimeters of hydrofluoric acid are added, enough to *just* dissolve the precipitate, and the liquid is evaporated to dryness. *No sulphuric acid is added.* The soluble fluorides, of iron and possibly titanium, are dissolved in a little water containing a few drops of hydrofluoric acid, and the insoluble rare earth fluorides are collected on a 5½-cm. filter, supported in a small rubber funnel. In these operations only platinum vessels can be used, because glass or porcelain would be attacked by the hydrofluoric acid.

The washed filter and contents are ignited in a platinum crucible, and a few cubic centimeters of dilute sulphuric acid are poured in. The contents of the crucible are then evaporated to dryness. The small mass is taken up with a little dilute hydrochloric acid, transferred to a small beaker, and the rare earths are precipitated as hydroxides with a slight excess of ammonia. The hydroxides are slightly washed and then dissolved on the filter in a little dilute hydrochloric acid, and precipitated with a decided excess of concentrated solution of ammonium oxalate. The oxalate is collected on a 5½-cm. filter, washed with water containing a little of this salt, ignited in a platinum crucible and weighed as $(Ce, Y)_2O_3$.[1]

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[1] Hillebrand, Bull. **700,** p. 176; Hillebrand–Lundell, pp. 755–756; Mellor, p. 502; M. Dittrich, Ber. Deutsch. Chem. Ges., **41,** p. 4373, 1908; J. Morozewicz, Bull. Acad. Sci., Cracovie, 1909, p. 207; Schoeller–Powell, p. 71.

[2] Hillebrand, Bull. **148,** p. 50.

[3] Cf. H. S. Washington, Trans. Am. Inst. Min. Eng., p. **755,** 1908; F. W. Clarke and H. S. Washington, U. S. Geol. Survey, Prof. Paper **127,** p. 22, 1924.

If the weight is more than a few milligrams the earths of the two main groups may be separated by dissolving the oxides in a very small volume of dilute hydrochloric acid, evaporating down almost to crystallization, adding a few drops of water, and, finally, a few cubic centimeters of cold *concentrated* solution of normal potassium sulphate. This should have been prepared beforehand, and must contain some undissolved potassium sulphate crystals. On standing, a double sulphate of potassium and cerium separates, as it is almost insoluble in the potassium sulphate solution, whereas the double sulphates of the metals of the yttrium group are easily soluble in it. The precipitate is filtered off on a small filter, washed with the concentrated potassium sulphate solution, dissolved in dilute hydrochloric acid, precipitated with ammonia, and the precipitate is ignited and weighed. The ignited oxide is the dioxide of cerium, CeO_2, of a dark, reddish-brown color. It may be calculated into the sesquioxide, Ce_2O_3, in which form the rare earths are stated in the analysis, by multiplying the weight by the factor 0.95, but the weight is usually so small as to make this an ultra-refinement.

The rare earths of the yttrium group may be determined by difference from the weight of the mixed oxides, or may be precipitated as hydroxides from the filtrate, ignited, and weighed as Y_2O_3. Further separation of the elements of the two groups is neither called for nor usually practicable. The weight of the rare earths is to be subtracted from that of the ammonia precipitate.

19. SULPHUR TRIOXIDE[2]

Sulphur trioxide, which may be present as a constituent of haüyne and nosean, both of which are soluble in hydrochloric acid, is determined in a separate portion of rock powder. About one gram of the powder is weighed out (p. 147) into a 250-c.c. beaker, and gently boiled with 50 c.c. of dilute hydrochloric acid (1:5). If pyrite or pyrrhotite is present, a stream of carbon dioxide should enter by the lip of the covered beaker, and fill the space beneath the cover before boiling is begun. It is, of course, continued during the boiling. In this way, any pyrite remains unattacked, while seven-eighths of the sulphur of pyrrhotite goes off as hydrogen sulphide, the remaining one-eighth being precipitated as sulphur. This need not be filtered off, as it is burned in the subsequent ignition.

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[1] The ignited precipitate is actually $m\ CeO_2 + n\ Y_2O_3$; but for the small quantities found in rocks it may be considered as given, since the reduction of CeO_2 to Ce_2O_3 is needless.

[2] Hillebrand, Bull. **700**, p. 233, Hillebrand–Lundell, p. 812.

After boiling for about a quarter of an hour, the liquid is filtered through a 9-cm. filter, and the residue and filter are washed. The volume of liquid should be about 200 c.c., to prevent precipitation of silica. It is then precipitated, while hot, with an excess of barium chloride solution, allowed to stand for an hour, the barium sulphate is filtered off, well washed, ignited, and weighed. To guard against contamination by silica it is always well to evaporate the ignited precipitate with a few drops of hydrofluoric and sulphuric acids, and again ignite. The weight of $BaSO_4$ is multiplied by 0.343 to obtain the weight of SO_3.

Before determining sulphur or sulphur trioxide, the condition in which the sulphur exists in the rock should be investigated. The microscope will usually reveal the presence of pyrite or pyrrhotite, as well as nosean or haüyne. If not, the rock powder should be boiled with a little dilute hydrochloric acid, and if hydrogen sulphide is evolved, the presence of pyrrhotite may be inferred, as the lazurite molecule is not apt to be found in rocks. A little of the filtered liquid may be tested with barium chloride for SO_3.

20. CHLORINE[1]

Chlorine may be present in rocks: (a) as water-soluble chlorides;[2] (b) in silicates soluble in nitric acid (sodalite, haüyne, apatite); or (c) in minerals insoluble in acid (scapolite).

To determine the first, one or two grams of the rock powder are extracted by boiling with 100 or 200 c.c. of water, and filtering. The filtrate is often turbid, which may be prevented by using double filters, or by the addition of a chlorine-free salt (such as sodium nitrate) to the liquid and to the wash-water. Very little washing is needed. Even if the turbidity persists, the filtrate is acidified with

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[1] Hillebrand, Bull. **700**, p. 220; Hillebrand–Lundell, pp. 798–800; Mellor, pp. 519, 652; Treadwell–Hall, p. 290.

[2] As from contamination by sea-water.

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a little chlorine-free nitric acid, boiled, and precipitated with a little silver nitrate. The mixture is allowed to stand overnight, so that the precipitate may be clear. If the filtrate was not turbid, the silver chloride is ignited in a small, weighed, *porcelain* or vitreosil crucible. As some of the silver chloride may have been reduced to metallic silver by the carbon, it is best to add a few drops of nitric acid, evaporate to dryness, and then add a few drops of hydrochloric acid, again evaporate to dryness and gently ignite. If the filtrate was turbid, the washed precipitate on the filter is ignited in a porcelain crucible, a little nitric acid is added, as above, but without evaporation to dryness, and the silver chloride is dissolved in a little warm ammonia, separated from the insoluble residue by filtration, and precipitated from the hot filtrate by acidifying with nitric acid.

14. If the chlorine is present in acid-soluble minerals (as is usually the case with igneous rocks) one gram of the rock powder is boiled with 100 c.c. of very dilute (1:20) chlorine-free nitric acid.[1] After filtration, the chlorine is precipitated in the filtrate by silver nitrate, and treated as above. The filtration may also be made in a Gooch crucible.

HF + H

only

no Pt.

If acid-insoluble silicates are present, or even in all cases, the rock powder may be boiled (in the platinum basin) with very dilute nitric and hydrofluoric acids. The liquid is filtered through paper in a small ~~rubber~~ funnel. The filtrate is caught in the platinum basin, or a Pyrex glass beaker will serve as it will be only slightly attacked by the very dilute hydrofluoric acid. The precipitation, filtration, and ignition of the silver chloride are carried out as above.

It is scarcely necessary to adopt the method of fusion with chlorine-free sodium carbonate, with subsequent leaching in hot water, and precipitation of the silver chloride after acidifying with nitric acid.

The weight of the AgCl, multiplied by 0.246, or 0.25 for the small amounts usually present, gives the weight of chlorine.

If the precipitate is very small, Hillebrand recommends that it be collected on a small paper filter, which is then dried, wound up in a weighed platinum wire, and carefully ignited. The increased weight of the wire is due to the metallic silver of the chloride that has alloyed with the platinum, and is multiplied by 0.33 to arrive at the weight of the chlorine.

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[1] The acid must be very dilute to prevent loss of chlorine.

21. Fluorine[1]

It is only in very exceptional rocks that fluorine occurs in more than one- or two-tenths of one per cent. Inasmuch as it is usually present only or mostly as a constituent of apatite, its amount may be calculated from that of the phosphorus pentoxide with sufficient accuracy for most purposes, as most apatites are fluor-apatite. But fluorine occurs, although in very small amount, in many biotites and hornblendes, as well as in fluorite; therefore, if these minerals are present the figure for fluorine calculated from that of P_2O_5 will be too low.

Fluorine is, of all the chemical constituents of rocks, one of the most difficult to determine with even approximate accuracy. Fortunately its determination may usually be dispensed with, as its amount is always very small, and its determination does not affect that of other constituents.

Fluorine may be determined either gravimetrically or colorimetrically. The errors incident to the gravimetric methods are, as Hillebrand says, "almost certain to be low and may even be negative when fluorine is present." A source of error is the loss of fluorine on ignition with paper. This is mentioned by Hillebrand, and for this reason Shepherd advocates the use of a Munroe crucible.[2]

For the small amounts of fluorine found in most igneous rocks, the colorimetric method is apparently the best.

Gravimetric Method.—The old gravimetric method of Berzelius is the one usually employed. In describing it here we follow the procedure of Treadwell-Hall and of Hillebrand, with some suggestions by Penfield.[3] The addition of silica is not necessary in the analysis of an igneous rock.

About 2 grams of the rock powder is fused with 10 grams of sodium carbonate. The cake is thoroughly leached with hot water, filtered and washed. The filtrate contains all the fluorine as alkali fluorides. About 3 grams of powdered ammonium carbonate is added to the filtrate, it is digested for an hour at 40° C., and when cold about one-half of this amount is again added.[4] The beaker is allowed to stand for about twelve hours, the precipitate is filtered off and washed with water containing ammonium carbonate. The excess of ammonium carbonate is destroyed in the filtrate by boiling (covered) and evaporating almost to dryness. A few drops of phenolphthalein are added and then *nitric acid* until the red color just disappears. The solution is now boiled, with the occasional addition of nitric acid if the red color reappears, and there is added 1 or 2 c.c. of a solution of zinc oxide in strong ammonium carbonate solution containing ammonia, which precipitates the last of the silica and some phosphorus. The liquid is now boiled until no more CO_2 or NH_3 is given off. The precipitate is filtered and washed a few times with water, the filtrate being received in a 400-c.c. beaker or, best, in the platinum basin.

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[1] Hillebrand, Bull. **700**, pp. 222–229; Hillebrand–Lundell, pp. 800–810; Mellor, pp. 637–640; Treadwell–Hall, p. 406.

[2] E. S. Shepherd, Jour. Geol., **33**, p. 313, 1925.

[3] Penfield and Howe, Am. Jour. Sci., **47**, p. 190, 1894; Penfield and Minor, ditto, p. 388. Cf. Hillebrand–Lundell, pp. 800–804.

[4] The ammonium carbonate precipitates the silica, alumina, etc.

As phosphoric acid is, and chromic acid may be, present, Hillebrand recommends the addition at this time of silver nitrate in excess, which will precipitate these substances. The liquid is heated and filtered, the excess of silver is precipitated by sodium chloride, again heated to coagulation and again filtered, when a little sodium carbonate is added to alkaline reaction. If no chromium or phosphorus is present, or only small amounts of these, the addition of silver nitrate may usually be dispensed with.

The heated filtrate, which contains alkali carbonate and fluoride, but which must not contain any ammonium salts, is precipitated by a large excess of calcium chloride.

The precipitate of calcium carbonate and fluoride is collected on a filter[1] and is washed with hot water. The precipitate is then washed into the platinum basin, (p. 38), leaving as little on the paper as possible. The paper is burned and ignited in a small platinum crucible and the ashes are added to the precipitate in the basin. The contents of the basin are evaporated to dryness, and then heated over a free flame to dull redness for a few minutes. If the platinum basin is not at hand the filter and paper are dried and the precipitate loosened from the paper as far as possible, and the paper is burned in a capacious crucible, to which the bulk of the precipitate is added. The crucible is then heated to dull redness for a few minutes.

A little water and 1 or 2 c.c. of acetic acid are poured into the basin or crucible (the vessel being covered to prevent loss from effervescence). When the action ceases the liquid is evaporated to dryness. Hot water is poured on the dry salts and the contents of the crucible or basin are filtered through a small filter and washed. The operation is repeated, using small quantities of acetic acid at a time,[1] the paper being separately ignited from the precipitate, until all the calcium carbonate and oxide are dissolved, as is shown by the absence of a residue on evaporating a few drops of the filtrate on platinum foil.

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[1] It is best to use a Munroe crucible, because ignition in paper causes loss of fluorine, although this will be negligible if the procedure described here is adopted.

If a Munroe or a similar crucible is used, the solution in dilute acetic acid, in small and repeated amounts, is always best done in this crucible. The final ignition is done in a Munroe or a Gooch or Vitreosil crucible, to avoid the loss caused by the ignition of the paper.

Finally the filter and purified calcium fluoride are gently ignited in the crucible and are weighed. Multiplication of the weight of CaF_2 by 0.49, or division by 2 in most cases, gives the weight of fluorine. For possible corrections see Hillebrand.

Fluorine may be determined gravimetrically also as lead chlorofluoride, PbClF,[2] for which the student may best consult Hillebrand-Lundell. It may also be determined volumetrically by decomposing the rock by the Berzelius method, adding a known weight of ferric chloride to the solution, and titrating the excess $FeCl_3$ iodimetrically[3] Small amounts of fluorine may be detected and it may also be determined by the use of alizarine or benzidine.[4]

Colorimetric Method.—Steiger[5] has proposed a colorimetric method for determining the small amounts of fluorine found in rocks, based on the bleaching effect of fluorine on hydrogen dioxide solutions of titanium, which has been modified by Merwin. The method in brief consists in fusing the rock with sodium carbonate, leaching with water, and adding a definite amount of standard titanium solution to the filtrate, which is compared colorimetrically with a fluorine-free titanium solution. The percentage of fluorine is shown by reference to a curve which has been determined empirically. For this and other details the student is referred to the original papers by Steiger and by Merwin, or to Hillebrand or Hillebrand-Lundell.

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[1] Penfield and Howe find that the use of much acetic acid at the start leads to loss of calcium fluoride.

[2] F. G. Hawley, Jour. Ind. Eng. Chem., **18,** p. 573, 1926; Hoffman and Lundell, Bur. Standards, Jour. Research, **3,** p. 581, 1929; Hillebrand–Lundell, pp. 603, 805.

[3] J. G. Fairchild, Jour. Washington Acad. Sci., **20,** p. 141, 1930.

[4] Leitmeier and Feigl, Tsch. Min. Pet. Mitth., **40,** p. 6, 1929.

[5] G. Steiger, Jour. Am. Chem. Soc., **30,** p. 219, 1908; Merwin, Am. Jour. Sci., **28,** p. 119, 1908; Hillebrand, Bull. **700,** pp. 227–229; Hillebrand–Lundell, pp. 807–810.

This method, which is only adapted to small amounts of fluorine, may be recommended for use in rock analysis for its rapidity, simplicity, and greater accuracy than the usual gravimetric methods. It may, however, be reiterated that it is seldom worth while to determine fluorine in rocks.

22. Carbon Dioxide[1]

Inasmuch as nearly all the minerals containing carbon dioxide that occur in igneous rocks are soluble in hydrochloric or nitric acid with evolution of carbon dioxide (dolomite and siderite only on warming), its presence may be easily shown by warming the rock powder with a little somewhat dilute nitric or hydrochloric acid, and noting whether effervescence ensues. This is done in a small test-tube. If there is no marked effervescence, one may make sure of the reaction, as Hillebrand suggests, by inclining the tube and examining the upper side with a lens for the stream of minute bubbles. Before the addition of the acid the powder should be stirred up well with warm water to drive out any mechanically attached air, bubbles of which might be mistaken for CO_2. If the rock contains considerable pyrrhotite the evolution of H_2S may be mistaken for that of CO_2, but the former is easily recognizable by its odor, as well as by the blackening of paper soaked in lead acetate solution to which a drop of ammonia has been added.

The determination of CO_2 is effected by the usual method, which is so well known that a brief description will suffice. It is inadvisable to use the compact but complicated and fragile forms of apparatus in which the CO_2 is determined by loss in weight; and this constituent should always be determined by direct weighing. If many determinations are to be made it is best to have the flask, condenser, and train of tubes permanently set up.

From 2 to 5 grams of the rock powder are weighed out accurately into a 250-c.c. Erlenmeyer flask provided with a two-hole stopper, and about 50 c.c. of hot water is poured in. The flask is secured in a clamp with space beneath for a Bunsen burner. A long-stemmed separatory funnel is passed through one hole of the stopper and an upward inclined small condenser through the other to retain most of the steam and hydrochloric acid from the flask.

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[1] Classen, **2**, pp. 653–656; Fresenius–Cohn, **1**, pp. 493–495; Hillebrand, Bull. **700**, pp. 217–219; Hillebrand–Lundell, pp. 623, 796; Mellor, pp. 553–555; Treadwell–Hall, pp. 330–333.

The condenser is connected with a train of U-tubes, as follows:[1] (1) a tube containing glass beads wet with concentrated sulphuric acid, to take up most of the water; (2) a tube containing pumice with anhydrous copper sulphate (p. 186), to remove any HCl or H_2S; (3) a tube containing a perchlorate desiccant or granular anhydrous calcium chloride;[2] (4) a tube containing soda-lime or, better, ascarite (soda-asbestos) (p. 67), this U-tube must have glass stop-cocks and is to be weighed; (5) a tube containing ascarite in the limb nearest to tube 4 and a desiccant in the other, this tube is also to be weighed; and (6) a large U-tube containing a desiccant in one arm and ascarite in the other, which finishes the train and acts as a precautionary trap for any water or CO_2 from the atmosphere.

The absorption tubes 4 and 5 are weighed to the nearest tenth milligram, after being carefully wiped dry. The rubber connections of the train should be as short as possible, since CO_2 passes rather freely through rubber.

Before these tubes 4 and 5 are put in place a cylinder or large U-tube filled with ascarite or soda-lime is attached to the separatory funnel by a perforated small stopper, and a current of air free from carbon dioxide is drawn hrough the system. The absoption tubes 4 and 5 are then put in place and 10 or 20 c.c. of dilute (1:1) hydrochloric acid is placed in the separatory funnel (stop-cock closed), and the stream of cold water in the condenser is started. The acid is allowed to enter the flask slowly if there is much carbon dioxide, rapidly if there is little. When effervescence ceases or diminishes, the current of CO_2-free air is started and the contents of the flask are heated to boiling. "The flame is kept low, so as to have steady but quiet ebullition, and the air current is not interrupted, although reduced to a slow rate." The gentle boiling is kept up for about fifteen minutes; then the flame is removed, and the aspiration is continued at an increased rate for another quarter of an hour.

The U-tubes 4 and 5 are then removed, closed, and allowed to become thoroughly cold in a large desiccator. This is necessary because the absorption of CO_2 gives rise to considerable heat. They are then weighed, the increase in weight being that of the CO_2 in the portion of rock powder taken.

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[1] A similar train is figured and described by Hillebrand–Lundell, Fig. 26, p. 623 and p. 624. They use a perchlorate desiccant instead of calcium chloride and ascarite (soda-asbestos) instead of soda-lime. It is best to use these new agents if they are procurable.

[2] Anhydrous calcium chloride is apt to contain calcium hydroxide, which will absorb CO_2. Therefore a stream of dry CO_2 should be passed for ten minutes through tubes containing it, and thoroughly washed out with CO_2-free air. This, however, may not be effective (Hillebrand–Lundell, p. 44). For this reason one of the perchlorate desiccants is much to be preferred.

If minerals that contain CO_2 and that are insoluble in acid, as some scapolites, are present, a little dilute hydrofluoric acid may be added to the acid used for the decomposition.[1]

23. CHROMIUM AND VANADIUM[2]

These constituents are so seldom present in appreciable amount in silicate rocks that the analyst will not often be asked to determine them.

Chromium should be determined in such rocks as dunites, peridotites, and pyroxenites, in which it occurs frequently. Some basalts also contain a little chromium. For this determination the colorimetric method as chromate is to be used. It is briefly summarized here.

If the filtrate from the leached sodium carbonate melt for sulphur, baria, and zirconia[3] is yellow, after addition of alcohol to destroy manganates, this may be used for the chromium determination. It is to be evaporated down to a bulk of less than 100 c.c., and the chromium is determined as described below. The total sulphur may be determined afterward in this solution by precipitation as barium sulphate (p. 256).

It is best, however, to determine chromium in a separate portion. About 2 grams of the rock powder are thoroughly fused with four times the weight of sodium carbonate, and the cake is extracted with water, as in the method for total sulphur (p. 256). A few drops of either ethyl or methyl alcohol are added to destroy the color of sodium manganate, and the liquid is filtered. If the yellow color is very faint the liquid should be concentrated to small bulk for use as the test solution, and placed in a small measuring flask of 25, 50, or 100 c.c., according to the depth of color. The standard solution is prepared by dissolving 0.255 gram of normal potassium chromate (K_2CrO_4) in a liter of water, the solution containing then 0.0001 gram of Cr_2O_3 per cubic centimeter.[3]

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[1] L. H. Borgstrom, Zeits. Anal. Chem., **53**, p. 685, 1914; Hillebrand, Bull. **700**, p. 219.

[2] Hillebrand, Bull. **700**, pp. 182–189; Hillebrand–Lundell, pp. 759–769; Mellor, pp. 467–485.

[3] See p. 68.

The depth of color of the test solution is then compared with that of the standard exactly as was done in the determination of titania (p. 192) or manganese by the colorimetric method. The results are very accurate for the small quantities found in rocks, indeed, more accurate than gravimetric methods.[1]

The determination of *vanadium* is so seldom necessary and the method is so complex, that it need not be given here. If it is desired to determine it, Hillebrand's method is to be used, a full description of which is given by him.[2]

It is to be remembered that the vanadium, as V_2O_5, is to be subtracted from the apparent percentage of P_2O_5, because it is precipitated with the phosphorus pentoxide as vanadomolybdate (p. 246).

Molybdenum may be determined in the portion used for vanadium. It is scarcely ever looked for, but if its determination is desired the method of Hillebrand[3] may be used.

24. Copper and Nickel[4]

If it is desired to determine copper, or other metals of the hydrogen sulphide group, which may rarely be present, it is advisable to use a separate portion, rather than to determine them in the sulphides remaining after the determination of manganese in the main portion, if the acetate method has been used. This is chiefly because in this they are contaminated with platinum, and partly because appreciable amounts of copper may have been introduced from the water-baths (Hillebrand).

A portion of about 2 grams is decomposed in a platinum basin with sulphuric and hydrofluoric acids, evaporated and heated to dryness, with possible repetition to drive off the HF (p. 251). About 10 c.c. of very dilute sulphuric acid is added and, after heating, the solution is filtered into a 250-c.c. Erlenmeyer flask. An excess of ammonia is added, and hydrogen sulphide is passed through to saturation, which precipitates the manganese, copper, nickel, and cobalt. A little more ammonia is added. The flask is filled to the neck, cooled, and allowed to stand overnight. The precipitate is collected on a small filter and washed with water containing ammonium chloride and ammonium sulphide. It is then extracted by hydrogen sulphide water, acidified with one-fifth of its volume of concentrated hydrochloric acid. Manganese passes into the filtrate.

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[1] Hillebrand, Bull. **700,** p. 183; Hillebrand–Lundell, p. 762.

[2] Hillebrand, Bull. **700,** pp. 184–189; Hillebrand–Lundell, pp. 764–766; Mellor, pp. 480–485; Treadwell–Hall, p. 282.

[3] Hillebrand; Am. Jour. Sci. (4), **6,** p. 209, 1898; Bull. **700,** p. 186; Hillebrand–Lundell, p. 765.

[4] Hillebrand, Bull. **700,** pp. 106, 136; Hillebrand–Lundell, pp. 740–743; Mellor, pp. 389–394; Treadwell–Hall, p. 149.

The filter with its precipitate is ignited in a *porcelain* or vitreosil crucible, the ash is dissolved in a few drops of aqua regia, and the solution is diluted with water in a small beaker. The copper[1] is precipitated by heating and passing H_2S. The CuS is filtered off and gently ignited in a porcelain crucible. A few drops of nitric acid are added, and after gentle heating and ignition, the copper is weighed as CuO.

About 2 grams of tartaric acid is added to the filtrate to hold up iron, and the nickel and cobalt are precipitated by passing H_2S. The liquid is rendered slightly acid with acetic acid and allowed to stand. The sulphides, ignited in porcelain, are weighed as oxides. The amount of cobalt in terrestrial rocks is always so small that it is not necessary to separate it from the nickel, but its presence may be established by testing with the borax bead.

The above is the somewhat elaborate procedure recommended by Hillebrand, but the copper may be more simply precipitated by H_2S in the first slightly acid filtrate and the nickel in the filtrate from the copper sulphide, by addition of ammonia, passing more H_2S, and a little acetic acid, with long standing, as explained above.

Nickel may also be determined as nickel glyoxime,[2] an excellent method, and one that is much used at the present time. This may be done either in the originally slightly acid solution of the rock powder is copper is not determined, or in the filtrate from the copper sulphide after driving off the H_2S by boiling.

About two grams of tartaric acid is added to hold up iron and the slightly acid solution is neutralized with ammonia. It is then heated nearly to boiling, and 5 to 10 c.c. of a 1 per cent solution of dimethylglyoxime is added. The volume of the alcohol should be less than half of the solution containing the nickel, because of the perceptible solubility of the precipitate in alcohol. Ammonia is added drop by drop, with stirring, until the liquid smells slightly of it, and it is allowed to stand overnight. The voluminous reddish precipitate is filtered hot through a weighed Gooch crucible. It is washed with hot water, *dried at 110° C.*, and weighed. The weight of the precipitate, which has the composition $Ni\ [(CH_3)_2 \cdot C_2NOH \cdot NO]_2$, is multiplied by the factor 0.258 to reduce it to NiO.[1] It may be well to note that nickel glyoxime sublimes at 250° C. with decomposition (Treadwell-Hall) so that it cannot be ignited to NiO.

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[1] There should be no platinum with this, as sulphuric acid was used for decomposition.

[2] L. Tschugaeff., Zts. Anorg. Chem., 46, p. 144, 1905; Hillebrand–Lundell, p. 313; Mellor, p. 394; Treadwell–Hall, p. 134.

25. Boron Trioxide[2]

Boron trioxide is seldom, if ever, determined in rocks, although it occurs as a constituent of tourmaline in some granites, and in metamorphic rocks that contain axinite, dumortierite, or danburite. Boron is also present in datolite, a secondary mineral often found with basalt and diabase, and search for it in such igneous rocks, or those that are connected with deposits of borates or with boric acid soffioni, would be of some theoretical interest. Boric oxide is also present in some glasses, such as Jena and Pyrex, so that a brief description of a reliable method for determining it is given here.

The direct and satisfactorily accurate determination of boron trioxide in silicates and silicate rocks, and in glasses, is somewhat difficult and tedious.[3] Allen and Zies, after thorough study of various methods, have decided that the method of Wherry, as modified by Sullivan and Taylor, cannot be recommended as one of high accuracy for general use. They found that the one devised by Chapin[4] is "superior to all others" for glasses and silicates. There is given here a brief summary of their description of the procedure, for details referring the student to their paper, or to the more accessible one by Chapin, or to Hillebrand-Lundell, (p. 614).

About one gram of the rock powder is fused with five or six times its weight of sodium carbonate and the cake is brought into solution by 1:1 hydrochloric acid in the platinum basin, exactly as in the treatment of the main portion, except that the amount of acid is kept as small as possible.

After dehydration of the unfiltered liquid by the addition of anhydrous calcium chloride, the boron trioxide, set free by the hydrochloric acid, is volatilized as methyl borate by passing the vapor of specially pure methyl alcohol through the hot liquid, and is collected by distillation. The solution of methyl borate in methyl alcohol so obtained is treated with an excess of sodium hydroxide to form sodium borate, which permits the removal of the methyl alcohol by distillation. The alkaline borate is treated with hydrochloric acid under proper conditions to expel CO_2. The excess HCl is neutralized with sodium hydroxide, using para-nitrophenol to indicate the end-point. Mannitol is now introduced, and the titration of the boric acid is carried out, using a few drops of phenolphthalein as indicator.

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[1] Or 0.203 for Ni.

[2] Hillebrand, Bull. **700**, pp. 234–241; Hillebrand–Lundell, pp. 611–617, 813; Mellor, pp. 578–589; Classen, **1**, pp. 609–614, (glass); Sullivan and Taylor, Jour. Ind. Eng. Chem., **6**, 897, 1914; Wherry and Chapin, Jour. Am. Chem. Soc., **30**, pp. 1687–1701, 1908; Allen and Zies, Jour. Am. Ceram. Soc., **1**, pp. 761–767, 779, 1918.

[3] The author is indebted to Dr. E. G. Zies, for aid in preparing this section.

[4] W. H. Chapin, Jour. Amer. Chem. Soc., **30**, p. 1691, 1908.

Allen and Zies found that it was always necessary to apply a correction, determined from an operation in blank under the same conditions. This would appear to be the only objection to the method, but the correction is always small and in a plus direction. The method is stated to be less tedious than might appear, and after the apparatus is once set up and the standard solutions are made, the determination can be carried out with fair rapidity.

26. Beryllia[1]

Although beryllium is seldom determined in igneous rocks,[2] it might well be looked for in granites connected with beryl-bearing pegmatites, and possibly in other sodic rocks, as there is reason to think that the high alumina reported in some nephelite syenites, not explicable by the mineral composition, may be due to the presence of unidentified beryl, which optically and crystallographically greatly resembles nephelite.[3] Beryllium has recently been found to be present in vesuvianite, in which its presence had not heretofore been suspected.[4]

For the determination of beryllia the method of Parsons and Barnes[5] is generally used. This depends on the solubility of beryllium hydroxide in a hot solution of sodium bicarbonate, in which the hydroxides of aluminum, iron, and titanium[6] are insoluble.

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[1] Hillebrand, Bull. **700**, p. 25; Hillebrand–Lundell, pp. 402–407; Mellor, pp. 448–450; Treadwell–Hall, p. 128 B; Schoeller and Powell, pp. 49–51. Cf. H. T. S. Britton, Analyst, **56**, p. 359, 1921; **47**, p. 50, 1922; L. Duparc, Bull. Soc. Franç. Min., **42**, p. 207, 1919.

[2] Only one case is noted by Washington in Prof. Paper **99**, (p. 164, No. 6), he has met with none since.

[3] H. S. Washington, Trans. Am. Inst. Min. Eng., **39**, p. 753, 1909.

[4] Palache and Bauer, Am. Mineral., **15**, p. 30, 1930.

[5] Parson and Barnes, Jour. Am. Chem. Soc., **28**, pp. 1589–1595, 1906.

[6] Rocks in which beryllia would be looked for contain very little titanium.

As applied to igneous rocks the procedure, in brief, is as follows: Two grams of the rock powder is fused with sodium carbonate, the silica is separated, and the alumina, etc., are precipitated by ammonia in the usual way, the precipitate carrying all the beryllia.[1] The precipitate is washed a few times with hot water containing about 5 per cent of ammonium acetate and a few drops of ammonia, *the presence of an electrolyte being necessary* to prevent the passing of colloidal beryllium hydroxide through the filter. The precipitate is dissolved on the filter, or as described on page 173, in as little as possible of warm dilute hydrochloric acid (1:2). The final solution should be about 100 c.c., colored with methyl red.

This is neutralized with ammonia, heated to boiling, and is slowly poured into about 100 c.c. of a nearly boiling solution of sodium bicarbonate ($NaHCO_3$) containing enough of this so that the mixed liquids will contain about 10 per cent of it. The whole is quickly brought to a boil, and is boiled for one-half to one minute.[2] The precipitate is filtered off and washed a few times with hot water *containing ammonium acetate.* The precipitate is dissolved on the filter with as little as possible of warm hydrochloric acid (1:2), and the precipitation and treatment with sodium bicarbonate with ammonia are repeated.

The combined cold filtrates, containing all the beryllium, but no aluminum, iron, or titanium, are carefully acidified with strong hydrochloric acid, the beaker being kept well covered to prevent loss, and the liquid is boiled to expel all CO_2.[3] The liquid is then precipitated in the cold with ammonia, brought *quickly* to a boil, and the beryllium hydroxide is filtered off (in paper) and washed with hot water containing ammonium acetate. It is ignited over a Meker burner to constant weight[4] and is weighed as BeO. This should always be dissolved in dilute hydrochloric acid and reprecipitated. The weight of the BeO is to be subtracted from that of the ignited ammonia precipitate. This method yields satisfactory results, but that with 8-hydroxyquinoline (p. 275) is to be preferred.

Several other methods for separating beryllium from aluminum, iron, and titanium have been proposed. Of these may be mentioned precipitation by tannin and ammonium acetate, the beryllium going into the filtrate.[1] Treatment of the dried hydroxide precipitate with hot glacial acetic acid,[2] in which beryllium acetate is soluble, would seem to be not well adapted to rock analysis. The same is true of Havens' separation by hydrochloric acid and ether saturated with hydrogen chloride.[3] Kolthoff[4] suggests the use of sodium fluoride to separate beryllium from aluminum and iron.

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[1] One precipitation is sufficient.

[2] The evolution of CO_2 must not be mistaken for boiling.

[3] *Complete expulsion of CO_2 is necessary* because beryllium hydroxide is soluble in ammonium carbonate.

[4] Ignited beryllia is more hygroscopic than alumina.

8-Hydroxyquinoline has recently been suggested to separate beryllium from aluminum, iron, and titanium.[5] The warm, *slightly acid* solution of the ammonia precipitate is treated with an excess of an acetic acid solution of 8-hydroxyquinoline, and a solution of $N/2$ ammonium acetate is slowly added until a permanent precipitate is formed; then 20–25 c.c. more of the ammonium acetate solution is added to insure complete precipitation of alumina, etc. Beryllium is precipitated in the filtrate heated nearly to boiling by the cautious addition of ammonia, and the beryllium hydroxide is washed with hot solution of ammonium acetate containing a few drops of ammonia. The precipitate may be colored yellow or brown by adsorbed hydroxyquinoline, but this is of no consequence. The precipitate is ignited to constant weight of BeO. Addition of oxalic acid prior to the ignition is not necessary (p. 209). This appears to be the best method for the separation of beryllium from aluminum. It seems scarcely necessary to convert the BeO into sulphate, $BeSO_4$, as suggested by the authors.

Colorimetric methods have been devised for the determination of beryllia by the use of curcumin[6] and quinalizarin[7] as indicators, but they need not be described here.

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[1] Moser and Niessner, Monatsh., p. 113, 1927; Moser and Singer, Monatsh., **48,** p. 673, 1927. Cf. Chem. Abstr., **22,** pp. 39, 742, 1928; Treadwell–Hall, 128 B.

[2] Parsons and Robinson, Jour. Chem. Soc., **28,** p. 557, 1906; Scholler and Powell, Anal. Rarer Elements, p. 49.

[3] F. S. Havens, Am. Jour. Sci., **4,** p. 111, 1897.

[4] I. M. Kolthoff, Jour. Am. Chem. Soc., **50,** p. 395, 1928.

[5] Kolthoff and Sandell, Jour. Am. Chem. Soc., **50,** pp. 1900–1904, 1928. Titanium is not mentioned by them, but it would be separated along with the aluminum and iron.

[6] I. M. Kolthoff, Jour. Am. Chem. Soc., **50,** p. 393, 1928.

[7] H. Fischer, Wiss. Veroff. Siemens–Konzern, **5,** Heft **2,** pp. 109–118, 1926.

APPENDICES

1. Factors for Calculation

Constituent	Sought	Found	Factor	Log
Baria	BaO	$BaSO_4$	0.66	9.8195
Ceria	Ce_2O_3	CeO_2	0.95	
Chlorine	Cl	$AgCl$	0.246	9.3927
Chlorine	Cl	Ag	0.33	
Copper	Cu	CuO	0.80	
Fluorine	F	CaF_2	0.49	
Fluorine	F	$PbClF$	0.06	
Iron oxides	FeO	Fe_2O_3	0.8998	9.9542
Iron oxides	Fe_2O_3	FeO	1.1113	0.0465
Lithia	Li_2O	Li_2SO_4	0.27	
Magnesia	MgO	$Mg_2P_2O_7$	0.3621	9.5588
Magnesia	MgO	Magnesium quinolate *	0.1291	9.1109
Manganous oxide	MnO	Mn_3O_4	0.93	9.9685
Manganous oxide	Mn_3O_4	MnO	1.08	0.0334
Nickel oxide	NiO	Nickel glyoxime †	0.258	9.4116
Phosphorus pentoxide	P_2O_5	$Mg_2P_2O_7$	0.6379	9.8048
Phosphorus pentoxide	P_2O_5	$24MoO_3 \cdot P_2O_5$	0.04	
Potash	KCl	K_2PtCl_6	0.3067	9.4868
Potash	K_2O	K_2PtCl_6	0.1938	9.2873
Potash	KCl	$KClO_4$	0.5381	9.7309
Potash	K_2O	$KClO_4$	0.3399	9.5314
Soda	Na_2O	$NaCl$	0.5303	9.7245
Soda	Na_2O	Na_2SO_4	0.4364	9.6399
Strontia	SrO	$SrSO_4$	0.56	9.7482
Sulphur	S	$BaSO_4$	0.1374	9.1379
Sulphur trioxide	SO_3	$BaSO_4$	0.343	9.5353
Vanadium oxide	V_3O_5	V_2O_3	1.2	
Zirconia	ZrO_3	$Zr_3P_2O_7$	0.43	9.6335

* $Mg(C_9H_6NO)_2$. † $NiC_8H_{14}O_4N_4$.

To obtain the weight of the substance sought, the weight of the substance found is multiplied by the appropriate factor. The factors are those given in Treadwell-Hall, *2*, pp. 746–753, 1928. They are based on the Table of International Atomic Weights, 1928.[1] They have been checked up and some additional factors are given. The decimals are carried out only as far as is deemed appropriate for the quantities usually found in igneous rocks, in the case of the less abundant constituents.

2. REFERENCES

The following books, most of them on quantitative analysis,[2] have been consulted and some of them are often cited. The name by which they are cited is given first, with the full title, author, etc. following, and brief remarks on some of the main features of the book.

BLASDALE.—The Fundamentals of Quantitative Analysis. W. C. Blasdale. D. Van Nostrand Co., New York, 1921, 403 pp. This book deals with quantitative analysis from the physico-chemical side. The theory of the chief operations is discussed, illustrated by brief descriptions of various types of determinations. An excellent book for the student. The treatment of silicates is, however, very inadequate and unsatisfactory.

CHESNEAU.—Principes Théoriques et Pratiques d'Analyse Minérale. G. Chesneau. Librairie Beranger, Paris, 1912, 641 pp. A general handbook on quantitative analysis, dealing with all the elements. It presents the methods generally in use in France. The analysis of silicates is treated very briefly.

CLASSEN.—Ausgewählte Methoden der Analytischen Chemie. Vieweg und Sohn, Braunschweig. Vol. I (the metallic elements), 1901, 940 pp. Vol. II (the non-metallic elements), 1903, 831 pp. This large and useful book contains good descriptions of well-selected methods for all the elements. It is now out of date, but is still a good book for reference.

DITTRICH.—Anleitung zur Gesteinsanalyse. M. Dittrich. Veit und Co., Leipzig, 1905, 98 pp. This, one of the earliest books on the analysis of rocks, gives some details of manipulation, but it neglects the minor constituents. It is now out of date.

FARNSWORTH.—The Theory and Technique of Quantitative Analysis. Marie Farnsworth. John Wiley & Sons, New York, 1918, 154 pp. This book treats of the usual analytical operations, with some discussion of the theory. About two-thirds of the volume is devoted to volumetric and potentiometric methods, for which last it is especially useful.

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[1] Jour. Am. Chem. Soc., **50**, p. 615, 1928.

[2] L. Duparc (Contribution à l'Analyse des Silicates Naturels, Bull. Soc. Franç. Minéral., 42, pp. 138–241, 1919), describes in some detail the methods used by him for the analysis of silicates and silicate rocks. This paper will be referred to in the text. His methods differ in several important details from those of Hillebrand and of the author.

Fresenius-Cohn.—Quantitative Analysis. C. R. Fresenius, trans. by A. I. Cohn. John Wiley & Sons, New York, 1904; Vol. I, 780 pp.; Vol. II, 1255 pp. The first volume deals with general inorganic quantitative analysis, the second with organic analysis and many special and commercial methods. A reprint of Hillebrand's Bulletin 176 is included in Vol. II. "Fresenius" is a classical work and was, in its day, most useful, but it is now quite out of date. The treatment of silicate analysis in Vol. I is very inadequate and unsatisfactory.

Fresenius-Mitchell.—Introduction to Qualitative Chemical Analysis. T. W. Fresenius, trans. by C. A. Mitchell. John Wiley & Sons, New York, 1921, 954 pp. This, the translation of the 17th edition of the well-known Fresenius, is a most useful work. It deals with all the elements, except those of the helium group, as well as with some organic substances. Unfortunately, all the references are confined to German publications, so that many of the most recent American papers are not cited.

Gooch.—Representative Procedures in Quantitative Chemical Analysis. F. A. Gooch. John Wiley & Sons, New York, 1916, 262 pp. This book describes many of the analytical operations in considerable detail. About one-half of it is devoted to volumetric analysis. The analysis of silicates is treated very inadequately.

Hillebrand.—The Analysis of Silicate and Carbonate Rocks. W. F. Hillebrand, U. S. Geological Survey, Bulletin **700**, Washington, 1919, 285 pp. This is the latest and revised reprint of former bulletins by the same author.[1] This excellent and classical treatise is the best book on the subject, written by the chemist who set the present high standard for the chemical analysis of rocks. It is intended for the experienced chemist, rather than for the beginner. Bull. **700** is incorporated, with revisions, in Hillebrand-Lundell.

Hillebrand-Lundell.—Applied Inorganic Analysis, with Special Reference to the Analysis of Metals, Minerals, and Rocks. W. F. Hillebrand and G. E. F. Lundell. John Wiley & Sons, New York, 1929, 929 pp. This excellent and very useful treatise describes the determination of almost all the elements (except those of the helium group). The procedures are described in considerable detail, there is some theoretical discussion, the most recent reagents are referred to, and there are many references to recent papers. This work, the most recent and complete treatise on general quantitative analysis, is frequently cited in the present book.

Jannasch.—Praktischer Leitfaden der Gewichtsanalyse. P. Jannasch. Veit & Co., Leipzig, Germany, 1904, 450 pp. The methods for the analysis of silicates are described at some length, with new methods devised by the author. The book is unsatisfactory and this edition is out of date.

Jakob.—Anleitung zur Chemischen Gesteinsanalyse. J. Jakob. Born-

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[1] No. **176**, 1900; No. **305**, 1907; No. **422**, 1910 and 1916. See also Bull. **148**, 1897.

traeger, Berlin, 1928, 81 pages. Methods, generally, those of Hillebrand and the author, but the descriptions are very brief and many unjustified modifications are introduced. The book "is distinctly disappointing," and cannot be recommended.

Kolthoff-Furman.—Volumetric Analysis. I. M. Kolthoff, trans. by N. H. Furman. John Wiley & Sons, New York; Vol. I, Theoretical Principles, 1928, 289 pp.; Vol. II, Practical Methods, 1929, 252 pp. Vol. I is for the advanced student. Vol. II describes in great detail all the most important methods of volumetric analysis, and is of great use for the student.

Mellor.—A Treatise on Quantitative Inorganic Analysis. J. W. Mellor. Griffin and Co., London, 1913, 778 pp. This excellent work is replete with descriptions of alternative methods, described in detail, with many references and useful hints and tables. It is devoted largely to the analysis of silicates, including rocks, clays, glasses, and glazes, with the determination of many elements not present in igneous rocks. It will be useful to every analyst as a work of reference, although this edition is not up to date.

Noyes.—A Course of Instruction in the Qualitative Analysis of Inorganic Substances. A. A. Noyes. The Macmillan Co., New York, 1923, 190 pp. This is a textbook to be used by the student under an instructor, rather than a book of reference. Many procedures are given in great detail and, although it is primarily devoted to qualitative analysis, the student will gain much useful information applicable to quantitative analysis.

Ostwald.—The Scientific Foundations of Analytical Chemistry. W. Ostwald. The Macmillan Co., New York, 1908, 207 pp. An excellent, short, and lucid discussion of the application of the principles of physical chemistry to the problems of quantitative chemical analysis. This seems to be the latest edition of the English translation.

Schoeller and Powell.—The Analysis of Minerals and Ores of the Rarer Elements. W. R. Schoeller and A. R. Powell. Griffin and Co., London, 1919, 239 pp. This book describes, in considerable detail, methods for the separation and determination of the rarer elements (except those of the helium group). A new edition would be welcome.

Scott.—Standard Methods of Chemical Analysis. W. W. Scott (Editor). D. Van Nostrand Co., New York, 1920, 898 pp. This voluminous work describes methods for the determination of almost all the elements, with the analysis of many commercial substances. It is intended for the use of industrial, rather than scientific, chemists. The procedures are described very briefly and the methods for the analysis of silicates are very inadequately treated.

Snell.—Colorimetric Analysis. F. D. Snell. D. Van Nostrand Co., New York, 1921, 150 pp. This is a useful but brief treatise. Most of the methods and procedures are described in some detail. It is now out of print.

Stieglitz.—The Elements of Qualitative Chemical Analysis. J. Stieglitz. Century Co., New York, Vol. I, Fundamental Principles, 1912, 312 pp.;

Vol. II, Laboratory Manual, 1911, 153 pp. This excellent book resembles that of Ostwald in presenting the application of the principles of physical chemistry to the methods of chemical analysis. Although it treats primarily of qualitative analysis, it is equally applicable to quantitative methods, and its discussions will be very useful for the student.

THORNTON.—Titanium, with Special Reference to the Analysis of Titaniferous Substances. W. Thornton, Jr. Chemical Catalog Co., New York, 1927, 262 pp. This book describes in great detail the procedures for the determination of titanium in a great variety of substances, including rocks.

TREADWELL-HALL.[1]—Analytical Chemistry; Vol. II, Quantitative Analysis. F. P. Treadwell, trans. by W. T. Hall. John Wiley & Sons, New York, 1928, 848 pp. This well-known and very useful work deals with all the common and some of the rarer elements. It describes many of the most recent methods, but the treatment of silicate analysis is too brief and too little detailed to be satisfactory. Although most of the references are to German publications, there are some to recent American literature.

TREADWELL-HALL.—Analytical Chemistry; Vol. I, Qualitative Analysis. F. P. Treadwell, trans. by W. T. Hall. John Wiley & Sons, New York, 1921, 597 pp. An excellent and very useful textbook, treating of nearly all the elements. Almost all of the references are to German papers, but a few are to the literature of other countries.

WASHINGTON.—Manual of the Chemical Analysis of Rocks. H. S. Washington. John Wiley & Sons, New York, 1919, 271 pp. The third edition of the present book is thus designated.

WASHINGTON.—Chemical Analyses of Igneous Rocks. U. S. Geological Survey, Professional Paper 99, Washington, 1917, 1201 pp. This collection of chemical analyses of igneous rocks is accompanied by a text, in which are discussed such topics as the character of rock analyses, including their accuracy, completeness, and representativeness, and the criteria by which to judge their quality. It also includes a description of the quantitative classification of igneous rocks. The large number of analyses recorded (8,602) will give the student many examples of excellence to be emulated, as well as many "horrible examples" that show to what depths the careless and incompetent analyst can descend.

YOE.—Photometric Chemical Analysis. Vol. I, Colorimetry. J. H. Yoe. John Wiley & Sons, New York, 1928, 771 pp. This very complete treatise deals with all the important elements and many organic compounds, with some biological analyses. The colorimetric procedures are described in detail, but the methods for the determination of titanium include only those for its presence in irons and steels, not in silicates or rocks.

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[1] The Quantitative Analysis (Vol. II) is meant when only "Treadwell-Hall" is referred to; Vol. I will be referred to as "Treadwell-Hall, Qual. Anal."

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